U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-271 969

Source Assessment Acrylonitrile Manufacture (Air Emissions)

Monsanto Research Corp, Dayton, Ohio

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, N C

Sep 77

PB 271 969

EPA-600/2-77-107j
September 1977

Environmental Protection Technology Series

SOURCE ASSESSMENT: ACRYLONITRILE MANUFACTURE (AIR EMISSIONS)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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NATIONAL TECHNICAL
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SPRINGFIELD, VA. 22161

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-77-107j	2.	3. RECIPIENT'S ACCESSION NO. PB-271 969
4. TITLE AND SUBTITLE SOURCE ASSESSMENT: Acrylonitrile Manufacture (Air Emissions)		5. REPORT DATE September 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T.W. Hughes and D.A. Horn		8. PERFORMING ORGANIZATION REPORT NO. MRC-DA-537
9. PERFORMING ORGANIZATION NAME AND ADDRESS Monsanto Research Corporation 1515 Nicholas Road Dayton, Ohio 45407		10. PROGRAM ELEMENT NO. 1AB015; ROAP 21AXM-071 11. CONTRACT/GRANT NO. 68-02-1874
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 5/74-7/77 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP task officer for this report is Irvin A. Jefcoat, Mail Drop 62, 919/541-2547. Related reports are also in the EPA-600/2-76-032 series.

16. ABSTRACT

The report gives results of an analysis of atmospheric emissions from propylene-based acrylonitrile manufacturing plants. Uncontrolled and controlled emission factors are given for each species emitted to the atmosphere from each source within a typical plant, based on field sampling data and engineering estimates. Emissions data are used to calculate several factors designed to quantify the hazard potential of the emissions. A detailed process description and flow sheet are presented for the SOHIO process. Present and future aspects of pollution control technology in the industry are discussed. Economic and production trends in the acrylonitrile industry and in each of the industries that are consumers of acrylonitrile are analyzed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Air Pollution Control	13B
Acrylonitrile	Stationary Sources	07C
Propylene	Source Assessment	
Industrial Processes	Emission Factors	13H
	SOHIO Process	

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 123
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PCA06 MFA01

EPA Form 2220-1 (9-73)

EPA-600/2-77-107j
September 1977

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Contract No. 68-02-1874
ROAP No 21AXM-071
Program Element No. 1AB015

EPA Task Officer: Irvin A. Jefcoat

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act, and the solid waste legislation. If control technology is unavailable, inadequate, uneconomical, or socially unacceptable, then financial support is provided for the development of the needed control techniques for industrial processes and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench- to full-scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on the basis of superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from acrylonitrile manufacture.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. In this study of acrylonitrile manufacture, Mr. Kenneth Baker, Mr. Edward J. Wooldridge, and Dr. I. Atly Jefcoat served as EPA Project Leaders.

This project was initiated under Task IX, Identification and Quantification of Toxic and Hazardous Emissions from Chemical Plants, of Contract 68-02-1320, Quick Reaction Engineering and Technical Services (Multiple Option Services Contract); it was continued and concluded under Contract 68-02-1874, Source Assessment.

ABSTRACT

Atmospheric emissions from propylene-based acrylonitrile manufacturing plants are analyzed. Uncontrolled and controlled emission factors are given for each species emitted to the atmosphere from each source within a typical plant based on field sampling data and engineering estimates. Emissions data are used to calculate several factors designed to quantify the hazard potential of the emissions. These include the source severity (defined as the ratio of time-averaged maximum ground level concentration of a pollutant to an acceptable concentration), industry contribution to total atmospheric emissions of criteria pollutants, and the population exposed to high contaminant levels from a representative plant. A detailed process description and flow sheet are presented for the SOHIO process. Present and future aspects of pollution control technology in the industry are discussed. Economic and production trends in the acrylonitrile industry and in each of the industries that are consumers of acrylonitrile are analyzed.

This report was submitted under Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1974 to July 1976 and the work was completed as of March 16, 1977.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AAQS --ambient air quality standard
ACN --acetonitrile
AN --acrylonitrile
SOHIO --The Standard Oil Company
TLV --threshold limit value

SYMBOLS

A --affected area, km^2
C --storage tank diameter factor
Cap --production capacity, metric tons/yr
C_i --production capacity of plant i, metric tons/yr
D --tank/reactor diameter, m
D_p --affected population density, persons/km^2
$\overline{D}_p$ --mean population density, persons/km^2
D_{p_i} --county population density for plant i, persons/km^2
e --2.72
E --emission factor, g/kg of product acrylonitrile
E' --emission factor, lb/ton of product acrylonitrile
F --hazard factor [primary AAQS for criteria pollutants; adjusted TLV otherwise (TLV x 0.33 x 0.01)], g/m^3
F_g --equivalent gasoline working loss, bbl/yr
F_p --paint factor
H --effective emission height, m
H' --tank outage, ft
K_T --turnover factor
L --total petrochemical loss, bbl/yr
L_1 --total petrochemical loss, lb/yr
L_g --total equivalent gasoline loss, bbl/yr
L_y --equivalent gasoline breathing loss, bbl/yr
MW --molecular weight, lb/lb-mole
n --number of plants
N --number of turnovers per year
P --pressure, kPa
P' --affected population, persons
Q --emission rate, g/s
Q' --propylene ratio, moles propylene/moles of gas
S --source severity
t, t_0 --averaging times, min
T --temperature, °C (or °F as indicated)
u --wind speed, m/s

ABBREVIATIONS AND SYMBOLS (continued)

SYMBOLS (continued)

$\bar{u}$ --average wind speed, m/s
v --superficial velocity, m/s
V --tank capacity, bbl
W --liquid density, lb/ft^3
x --downwind distance from source, m
y --horizontal distance from centerline of dispersion, m
Y --yield, %
ΔT --average ambient temperature change, °F
π --3.1416
σ_y --standard deviation of vertical dispersion
σ_z --standard deviation of horizontal dispersion
$\underline{\chi}$ --downwind ground level concentration, g/m^3
χ --average concentration, g/m^3
χ_{max} --maximum ground level concentration, g/m^3
$\bar{\chi}_{max}$ --time-averaged maximum ground level concentration, g/m^3
$\bar{\chi}(x)$ --annual mean ground level concentration, g/m^3

SECTION I

INTRODUCTION

Acrylonitrile is an important synthetic organic chemical used in the manufacture of acrylic fibers, nitrile rubber, and plastic resins, and as a chemical intermediate. Present (1976) annual production capacity in the United States is 8.62 x 10^5 metric tons[a] (9.5 x 10^5 tons). Acrylonitrile is produced by the catalytic vapor phase ammoxidation[b] of propylene. This document presents a detailed study of acrylonitrile manufacturing plants from the standpoint of atmospheric emissions and their potential environmental impact.

The major results of this study are summarized in Section II. These results include emission factors for each species emitted to the atmosphere from each emission point within a representative acrylonitrile plant. Also tabulated are several factors designed to measure the environmental hazard potential of acrylonitrile plant operations including: source severity, the industry contribution to total atmospheric emissions of criteria pollutants, the population affected by a representative plant, and future trends in emissions.

Section III describes the acrylonitrile manufacturing process in detail. Discussion is limited to the SOHIO process since it is the only one currently used in the U.S. Included are descriptions of each major processing step, flow diagrams, process chemistry, and material and energy balances.

Atmospheric emissions from acrylonitrile manufacturing plants are discussed in Section IV. The species known to be emitted and/or produced by each process step are detailed, and each emission point within the plant is described. Compositions and flow rates of streams emitted to the atmosphere are provided. A representative acrylonitrile plant is defined, and emission factors are given for such a plant. These emission factors are then used to determine the source severity, calculate the industry contribution to total emissions of criteria pollutants, estimate the affected population, and determine future trends in emissions.

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[a] 1 metric ton = 10^6 grams = 2,205 pounds = 1.1 short tons (short tons are designated "tons" in this document); conversion factors and metric system prefixes are presented at the end of this report.

[b] Ammoxidation is the oxidation of a chemical in the presence of ammonia.

Present and future aspects of pollution control technology in the acrylonitrile industry are considered in Section V. Several process modifications are described which have been used in recent years and shown to have reduced the environmental impact of the atmospheric emissions from the industry.

Production trends in the acrylonitrile industry are addressed in Section VI. The trends in each of the industries that are major consumers of acrylonitrile are also analyzed. Finally, estimates of acrylonitrile production through the remainder of the present decade are discussed.

SECTION II

SUMMARY

Acrylonitrile is manufactured by the catalytic vapor phase ammoxidation[a] of propylene using the SOHIO process developed by The Standard Oil Company (SOHIO). There are six plants operating in the U.S. having a combined production capacity of 8.62×10^5 metric tons/yr (9.5×10^5 tons). The plants are located in rural and nonrural counties having population densities of 29 to 1,103 persons/km^2 (73 to 2,758 persons/mi^2).

Sources of atmospheric emissions within acrylonitrile plants include the absorber vent, incinerator stack, flare stack, deep well pond, storage tanks, product transport loading facility and fugitive sources. Materials emitted from acrylonitrile plants include criteria pollutants (carbon monoxide, hydrocarbons, nitrogen oxides and sulfur oxides) and 23 chemical substances (such as propylene, propane, acrylonitrile, acetonitrile, hydrogen cyanide, benzene, and toluene).

The absorber vent gas consists of neutralized reactor effluent which has been scrubbed for nitriles recovery. This stream accounts for more than 99.9% of uncontrolled carbon monoxide emissions and 87.3% of the uncontrolled hydrocarbon emissions. Current methods of emissions control for these emissions involve the use of combustion equipment which has demonstrated greater than 95% removal of both carbon monoxide and hydrocarbons.

The incinerator stack gas consists of combustion products from the thermal oxidation of acetonitrile waste and hydrogen cyanide waste. Emissions from the incinerator consist of nitrogen oxides, sulfur oxides and hydrogen cyanide. Combustion of nitrile feed to the incinerator is greater than 99% complete; only 0.6% of the nitrile feed is converted to NO_x.

The acrylonitrile plant flare is used for the combustion of hydrocarbon releases from the purification section. Approximately 90% combustion of carbon monoxide and 75% to 80% combustion of hydrocarbons are obtained according to previous studies performed by Houdry Division, Air Products and Chemicals, Inc.

---

[a] Ammoxidation refers to the oxidation of a substance in the presence of ammonia.

Ultimate disposal of acrylonitrile wastewater is performed through the use of deep injection wells. A nonaerated lagoon (deep well pond) is used for solids removal prior to deep well injection. The deep well pond is a source of hydrocarbon emissions due to the volatile organics contained in the wastewater. Attempts to reduce the hydrocarbon emissions have involved the use of a layer of lube oil over the pond. This action reduces the deep well pond hydrocarbon emissions by >92%.

Storage tanks contain refined and crude acrylonitrile. Available control devices in use include conservation vents, vent condensers, and floating roofs. Emissions from the product transport loading facility occur during the loading of railcars and tank trucks. Emission controls include the use of activated carbon adsorption and refrigeration compression systems.

Fugitive emission losses occur at pump seals, flanges, gaskets, pressure relief valves, compresser seals, and valves.

Emission factors are summarized in Tables 1 and 2 for uncontrolled and controlled emissions from acrylonitrile plants. The absorber vent is controlled at three acrylonitrile plants, as is the deep well pond. None of the other emission vents are controlled at acrylonitrile plants.

To assess the environmental impact of atmospheric emissions from acrylonitrile manufacture, the source severity for each material emitted from each emission point was estimated. Source severity is defined as the pollutant concentration to which the population may be exposed divided by an "acceptable concentration." The exposure concentration is the time-averaged maximum ground level concentration as determined by Gaussian plume dispersion methodology. The "acceptable concentration" is that pollutant concentration at which an incipient adverse health effect is assumed to occur. For criteria pollutants, it is the corresponding primary ambient air quality standard. For noncriteria pollutants, it is a surrogate air quality standard determined by reducing TLV's for chemical substances using an appropriate safety factor. Source severities were calculated for a representative plant defined as having a production capacity of 1.4×10^5 metric tons/yr (1.54×10^5 tons/yr).

The results show that the deep well pond has the highest source severity (98 for total uncontrolled hydrocarbons) even though it represents only 18.3% of the total mass of uncontrolled hydrocarbon emissions. Its source severity is highest because the deep well pond is a ground level source while all other emission points are elevated point sources.

The maximum source severity for the elevated point sources is 10.4 for uncontrolled hydrocarbon emissions from the absorber vent. Propylene and propane comprise 96% of the hydrocarbons in the

TABLE 1. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (UNCONTROLLED EMISSIONS)
(g/kg of acrylonitrile produced)

	Emission point						
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Storage tanks
Criteria pollutants							
Carbon monoxide	79.3 ± 6%	0.0040 ± 10%					
Hydrocarbons (as CH_4)[a]	57.1 ± 7%	0.0203 + 428% − 100%	0.268	13 ± 61%	0.00038 ± 20%	0.0055 ± 20%	0.661 ± 20%
Nitrogen oxides		0.542 + 107% − 100%	0.01				
Sulfur oxides		0.176 ± 59%					
Particulates							
Chemical substances							
Methane	0.67 ± 6%	0.0023 ± 10%					
Ethane	1.93 ± 92%						
Ethylene	2.57 ± 81%						
Propane and propylene	55.0 ± 60%		0.022		0.000006 ± 20%		
Butene	0.400 ± 50%						
Benzene	0.146 ± 50%						
Toluene	0.065 ± 50%						
Acrylonitrile	0.039 ± 41%	<0.0015	0.039		0.00042 ± 20%	0.0065 ± 20%	0.802 ± 20%
Acetonitrile	0.625 ± 49%	<0.0015			0.000024 ± 20%		
Hydrogen cyanide	0.275 ± 22%	0.0343 + 428% − 100%	0.35				
Fumaronitrile				0.036			
Pyridine				5.2 ± 74%			
Propionaldehyde	0.0061 ± 50%						
Furan	0.467 ± 50%						
Ammonia					0.000006 ± 20%		
Allyl alcohol	0.024 ± 50%						

---

[a] Emission factors for total hydrocarbons do not equal the sum of emission factors for all organic materials except methane. To determine the hydrocarbon emission, the methane equivalent emission factors (based on carbon) for each nonmethane organic material are calculated and then summed. (Statement applies to all emission points except deep well pond where 7.8 g/kg of material [two species] were unidentifiable.)

Note: Blanks indicate no emissions present.

TABLE 2. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (CONTROLLED EMISSIONS) (g/kg)

	Emission point	
Material emitted	Absorber vent[a]	Deep well pond[b]
Criteria pollutants		
Carbon monoxide	<4.0	
Hydrocarbons	<2.86	1.1 + 117% - 100%
Nitrogen oxides		
Sulfur oxides		
Particulates		
Chemical substances		
Methane	<0.03	
Ethane	<0.1	
Ethylene	<0.1	
Propane and propylene	<3.0	
Butene	<0.02	
Butane		0.06 + 182% - 100%
Methanol		0.16 + 138% - 100%
Pentane		0.04 + 172% - 100%
Acetaldehyde		0.06 + 422% - 100%
Hexane		0.04 + 145% - 100%
Ethanol		0.1 + 345% - 100%
Benzene	<0.07	0.1 + 150% - 100%
Toluene	<0.003	0.02 + 222% - 100%
Acrylonitrile	<0.002	
Acetonitrile	<0.03	
Hydrogen cyanide	<0.01	
Propionaldehyde	<0.0003	
Furan	<0.02	
Allyl alcohol	<0.001	

Note: Blanks indicate no emissions present.

[a] Control efficiency is >95% for thermal oxidizers or catalytic incinerators for the carbon monoxide and hydrocarbon emissions from absorber vent.

[b] Control efficiency is 92% when using a lube oil covering on pond for control of hydrocarbons.

absorber vent gas. For absorber vents using thermal oxidizers to control hydrocarbon emissions, the hydrocarbon source severity is <0.52 when obtaining >95% removal of the hydrocarbons. Source severities for uncontrolled and controlled emissions are shown in Tables 3 and 4.

TABLE 3. SOURCE SEVERITIES FOR UNCONTROLLED EMISSIONS

	Emission point						
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond[a]	Fugitive emissions	Product transport loading facility	Storage tanks
Criteria pollutants							
Carbon monoxide	0.07	0.000013					
Hydrocarbons[b,c]	10.4	0.002	0.075	98	0.0039	0.0040	2.48
Nitrogen oxides		0.48	0.0023				
Sulfur oxides		0.0035					
Particulates							
Chemical substances							
Methane	0.0058	0.000051					
Ethane	0.0088						
Ethylene	0.013						
Propane and propylene	0.18		0.0001		0.000001		
Butene	0.0010						
Acetaldehyde							
Benzene	0.03[d]						
Toluene	0.001						
Acrylonitrile	0.0054	0.00073	0.0054		0.0028	0.043	1.70
Acetonitrile	0.055	0.00047			0.000048		
Hydrogen cyanide	0.15	0.068	0.200				
Fumaronitrile				–[e]			
Pyridine				202			
Propionaldehyde	0.013						
Furan	0.145						
Ammonia					0.000035		
Allyl alcohol	0.030						

[a] Occurs on plant property.

[b] Hydrocarbons include all organic materials except methane.

[c] Total source severity for nonmethane organic materials will not equal the source severity for hydrocarbons. Source severities for the organic chemicals are based on the toxicity of the chemicals. The hydrocarbon source severity is based on the toxicity of oxidants, which are the products of the photochemical degradation of the organic chemicals.

[d] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene becomes 900.

[e] Indeterminate since a TLV does not exist for this material.

TABLE 4. SOURCE SEVERITIES FOR CONTROLLED EMISSIONS

	Emission point	
Material emitted	Absorber vent[a]	Deep well pond[b,c]
Criteria pollutants		
Carbon monoxide	<0.0035	
Hydrocarbons	<0.52	7.8
Nitrogen oxides		
Sulfur oxides		
Particulates		
Chemical substances		
Methane	<0.005	
Ethane	<0.00044	
Ethylene	<0.00065	
Propane and propylene	<0.009	
Butene	<0.00005	
Butane		0.0068
Methanol		0.18
Pentane		0.0065
Acetaldehyde		0.097
Hexane		0.032
Ethanol		0.015
Benzene	<0.0015[d]	0.15[e]
Toluene	<0.00005	0.016
Acrylonitrile	<0.00027	
Acetonitrile	<0.048	
Hydrogen cyanide	<0.0075	
Propionaldehyde	<0.00065	
Furan	<0.0073	
Allyl alcohol	<0.0015	

Note: Blanks indicate no emissions present.

[a] Control efficiency >95% for thermal oxidizers or catalytic incinerators for the carbon monoxide and hydrocarbon emissions from absorber vent.

[b] Control efficiency >92% when using a lube oil covering on pond for control of hydrocarbons.

[c] Occurs on plant property.

[d] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene is <4.5.

[e] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene becomes 300.

Atmospheric emissions of criteria pollutants from acrylonitrile plants in the U.S. in 1976 amount to 26,900 metric tons (29,600 tons) of carbon monoxide, 24,900 metric tons (27,400 tons) of hydrocarbons, 470 metric tons (517 tons) of nitrogen oxides, and 15.0 metric tons (16.5 tons) of sulfur oxides. These values equal 0.03%, 0.15%, 0.005%, and <0.001%, respectively, of the total U.S. emissions of carbon monoxide, hydrocarbons, nitrogen oxides, and sulfur oxides from stationary sources.

Hydrocarbon emissions from acrylonitrile manufacture in Louisiana, Ohio, Tennessee, and Texas amounted to 0.64%, 0.78%, 3.57%, and 0.12% of the total hydrocarbon emissions of these states, respectively. Carbon monoxide emissions from acrylonitrile manufacture in Louisiana, Ohio, Tennessee, and Texas amounted to 0.97%, 0.05%, 4.62%, and 0.115%, respectively.

Acrylonitrile production in 1973 was 6.13×10^5 metric tons (6.74×10^5 tons) and is expected to be 1.3×10^6 metric tons (1.4×10^6 tons) in 1978. This represents an increase of 112% over the 5-year period. During this period, the national masses of carbon monoxide and hydrocarbon emissions from the absorber vent are expected to decrease 58% and 56%, respectively, because of state regulations controlling these emissions.

The number of persons that may be exposed to concentrations above the primary ambient air quality standard[a] for uncontrolled hydrocarbon emissions from the representative acrylonitrile plant is 13,300. Approximately 96% of this exposure is due to propylene and propane. When controlling hydrocarbons by 95%, the number of persons possibly exposed to concentrations exceeding the primary ambient air quality standard is zero. Based on the definition of source severity for chemical substances in this document, no persons are exposed to concentrations of nitrile emissions exceeding 0.0033 times the threshold limit value, g/m^3.

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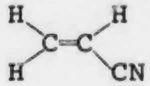
[a] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons in this report is a recommended guideline for meeting the primary ambient air quality standard for photochemical oxidants.

SECTION III

SOURCE DESCRIPTION

A. PROCESS DESCRIPTION

Acrylonitrile, a colorless liquid with a mild odor, freezes in the range of -83°C to -84°C and boils in the range of 77.3°C to 77.4°C. Synonyms for acrylonitrile include propenenitrile and vinyl cyanide. The structure of acrylonitrile is:



Acrylonitrile can be produced using the following methods: (1) oxidation of propylene in the presence of ammonia (ammoxidation of propylene) using either a bismuth phosphomolybdate or uranium-based catalyst; (2) addition of hydrogen cyanide to acetylene using a cuprous chloride catalyst; (3) catalytic reaction of propylene with nitric oxide; (4) reaction of ethylene oxide with hydrogen cyanide followed by catalytic dehydrogenation of ethylene cyanohydrin; and (5) ammoxidation of propane.[1,2]

Each of the first four processes listed above has been used commercially, and ammoxidation of propane has been studied on a pilot scale. However, since 1971 the ammoxidation of propylene is the only process which has been used commercially. The process is patented by The Standard Oil Company (SOHIO) and is known as the SOHIO process.

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[1] Hawley, G. G. The Condensed Chemical Dictionary, Eighth Edition. Van Nostrand Reinhold Company, New York, New York, 1971. p. 15.

[2] Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Vol. 1. John Wiley & Sons, Inc., New York, New York, 1969. pp. 338-351.

This source description will be limited to the SOHIO process because it is the only commercial process in use. Figure 1 is a schematic flow diagram for a representative acrylonitrile plant.[3]

Streams numbered in Figure 1 are defined in Table 5. The process consists of the following steps: (1) feed materials storage and preparation; (2) processing and product recovery; (3) product purification; (4) wastes disposal; and (5) product storage and transportation. Each of these topics is described in the following subsections.

1. Feed Materials Storage and Preparation

Feed materials used in the acrylonitrile process are propylene, ammonia, and air.

Propylene feed (stream 1 in Figure 1) consists of a propylene/propane mixture with a propylene content of 90% to 97% on a mass basis (personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974). The source of propylene is either refinery production or steam crackers which are located near each plant site. Propylene is stored as a liquid at its vapor pressure of 1,050 kPa at 21°C. This feed is vaporized and preheated using process steam prior to use for acrylonitrile manufacture.

Agricultural-grade ammonia[3] (stream 2) of the following composition[4] is used in the manufacture of acrylonitrile:

Component	Amount
Ammonia	99.8% by wt (minimum)
Water	0.015% by wt (maximum)
Oil	3 ppm (maximum)
Noncondensable gas	0.0002 m^3/kg (maximum)

The ammonia is stored as a liquid at its vapor pressure of 890 kPa at 21°C. It is vaporized and preheated using process steam prior to use.

Air (stream 3) is filtered and compressed prior to use.

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[3] Schwartz, W. A., F. B. Higgins, Jr., J. A. Lee, R. Newirth, and J. W. Pervier. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume 2: Acrylonitrile Manufacture. EPA-450/3-73-006-b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. February 1975. 103 pp.

[4] Considine, D. M. Chemical and Process Technology Encyclopedia. McGraw-Hill Book Company, New York, New York, 1974. p. 108.

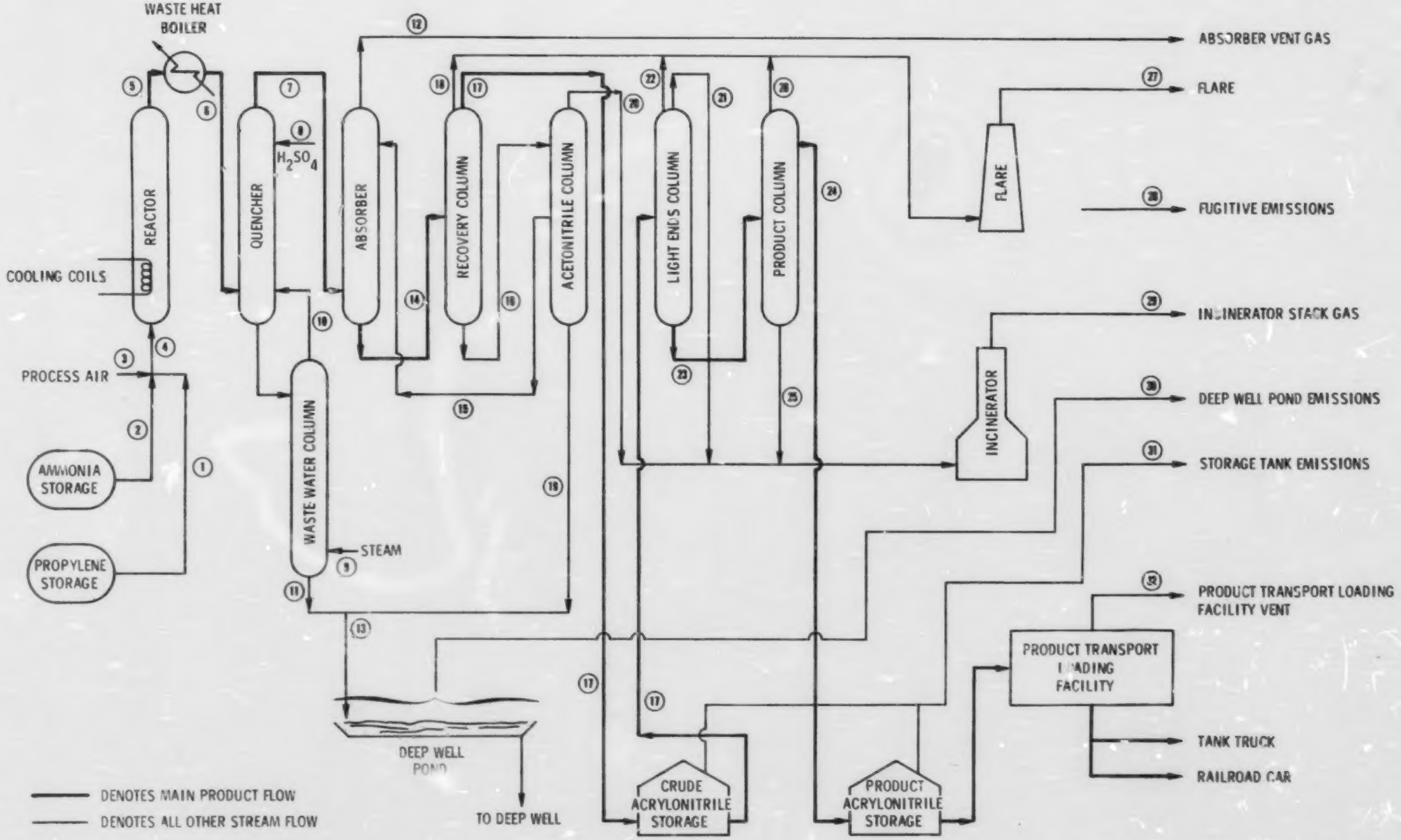
WASTE HEAT BOILER
REACTOR
COOLING COILS
PROCESS AIR
AMMONIA STORAGE
PROPYLENE STORAGE
QUENCHER
H_2SO_4
WASTE WATER COLUMN
STEAM
ABSORBER
RECOVERY COLUMN
ACETONITRILE COLUMN
LIGHT ENDS COLUMN
PRODUCT COLUMN
DEEP WELL POND
TO DEEP WELL
CRUDE ACRYLONITRILE STORAGE
PRODUCT ACRYLONITRILE STORAGE
FLARE
INCINERATOR
PRODUCT TRANSPORT LOADING FACILITY
ABSORBER VENT GAS
FLARE
FUGITIVE EMISSIONS
INCINERATOR STACK GAS
DEEP WELL POND EMISSIONS
STORAGE TANK EMISSIONS
PRODUCT TRANSPORT LOADING FACILITY VENT
TANK TRUCK
RAILROAD CAR
DENOTES MAIN PRODUCT FLOW
DENOTES ALL OTHER STREAM FLOW
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Figure 1. Flow diagram for a representative acrylonitrile plant.[3]

TABLE 5. STREAM CODES FOR FIGURE 1

Stream number	Description
1	Propylene feed
2	Ammonia feed
3	Process air
4	Reactor feed
5	Reactor product
6	Cooled reactor product
7	Quenched reactor product
8	Sulfuric acid
9	Stripping steam
10	Wastewater column volatiles
11	Wastewater column bottoms
12	Absorber vent gas
13	Acrylonitrile plant wastewater
14	Absorber bottoms
15	Water recycle
16	Crude acetonitrite
17	Crude acrylonitrile
18	Recovery column purge vent
19	Acetonitrite column bottoms
20	Acetonitrile
21	Hydrogen cyanide
22	Light ends column purge vent
23	Light ends column bottoms
24	Product acrylonitrile
25	Heavy ends
26	Product column purge vent
27	Flare
28	Fugitive emissions
29	Incinerator stack gas
30	Deep well pond emissions
31	Storage tank emissions
32	Product transport loading facility vent

2. Processing and Product Recovery

a. Reactor--

In the SOHIO process, propylene/ammonia/air reactants are fed in approximately the molar ratio of 1/1.06/8.40.[3] Stoichiometric proportions would be 1/1/7.14 as dictated by the chemical equation:

$$CH_2CHCH_3 + NH_3 + 1.5O_2 + 5.64N_2 \rightarrow CH_2CHCN + 3H_2O + 5.64N_2 \quad (1)$$

However, 3% excess ammonia is used to force the reaction toward completion, and 18% excess air is used to continuously regenerate the catalyst.[3]

The reactants are fed continuously to the reactor, which operates at 135 kPa to 310 kPa at 400°C to 510°C. This is a gas fluidized bed reactor in which the catalyst is the solid phase and the reactants and products comprise the vapor phase.

Details of the reactor design have not been published in domestic technical journals. However, two SOHIO patents describe the reactor design (U.S. 3,427,343[5] and Belgian 700,641[6]). The U.S. patent states that stacked multistage fluidized bed reactors having at least four catalyst compartments are preferred. In each compartment the catalyst is fluidized by passing gases through trays having 33% open area provided by 4.8-mm diameter holes. Catalyst fines are collected by internal cyclones at the top of the reactor and returned to the lowest catalyst compartment. Propylene and ammonia are introduced into the third catalyst compartment from the bottom while air is added to the lowest catalyst compartment. Sufficient air is used to maintain 2% to 3% oxygen concentration in the reactor effluent gases. By using the lower compartments for contacting the catalyst with oxygen and by controlling the outlet oxygen concentration, catalyst regeneration becomes continuous.

The performance of a 3.3-m diameter, 10-stage reactor using a uranium-based catalyst (catalyst 21) is described in the patent.[5] The catalyst has the physical properties shown in Table 6. When reactor conditions were changed to allow the ammonia and propylene to enter with the air in the lower compartment, the yield began dropping almost immediately.[5]

The second SOHIO patent[6] describes details of the upper part of the reactor where the solid is disengaged from the gas. If this part of the reactor is incorrectly designed, masses of catalyst will adhere to the upper metal surface. Because of poor gas circulation through the mass, temperatures will rise and damage the catalyst. Catalyst chunks may break off and fall into the dense bed below, causing inefficient reaction conditions with attendant loss of yield. In the preferred reactor design shown in Figure 2, nitrogen is added to the uppermost chamber and flows through the cyclone support plate. Nitrogen and the reaction gases from the compartments below are then discharged into a series of three cyclones where catalyst is removed and returned to the reactor below, while the gases are allowed to exit.

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[5] Callahan, J. L., E. C. Milberger, and R. K. Grasseli. Process for Preparing Olefinically Unsaturated Aldehydes and Nitriles. U.S. Patent 3,427,343 (to The Standard Oil Company), February 11, 1969.

[6] Callahan, J. L., R. D. Presson, and A. F. Miller. Cylindrical, Vertical, Fluidized Solid Reactor. Belgian Patent 700,641 (to The Standard Oil Company), December 28, 1967.

TABLE 6. PERFORMANCE OF A PILOT-SCALE ACRYLONITRILE REACTOR [5]

Catalyst Properties

Property	Value
Apparent bulk density	1,196 kg/m^3
Compact bulk density	1,361 kg/m^3
Pore volume	0.000218 m^3/kg
Surface area	18 m^2/g

Catalyst Particle Size Distribution

Particle size, μm	Weight %	Cumulative weight %
$\geq$105	16	16
<105 to 88	12	28
<88 to 74	21	50
<74 to 63	7	56
<63 to 53	6	62
<53 to 44	19	81
<44	19	100

Reactor Performance Data

Temperature = 480°C
Contact time = 10 s
Pressure = 205 kPa

Hours on stream	Yield,[a] %
6	67.3
11	66.9
20	66.9
28.5	67.1
75	67.4
95	68.2

[a] Yield is defined as the kilograms of carbon in acrylonitrile product divided by the kilograms of carbon in the propylene feed and expressed as a percent.

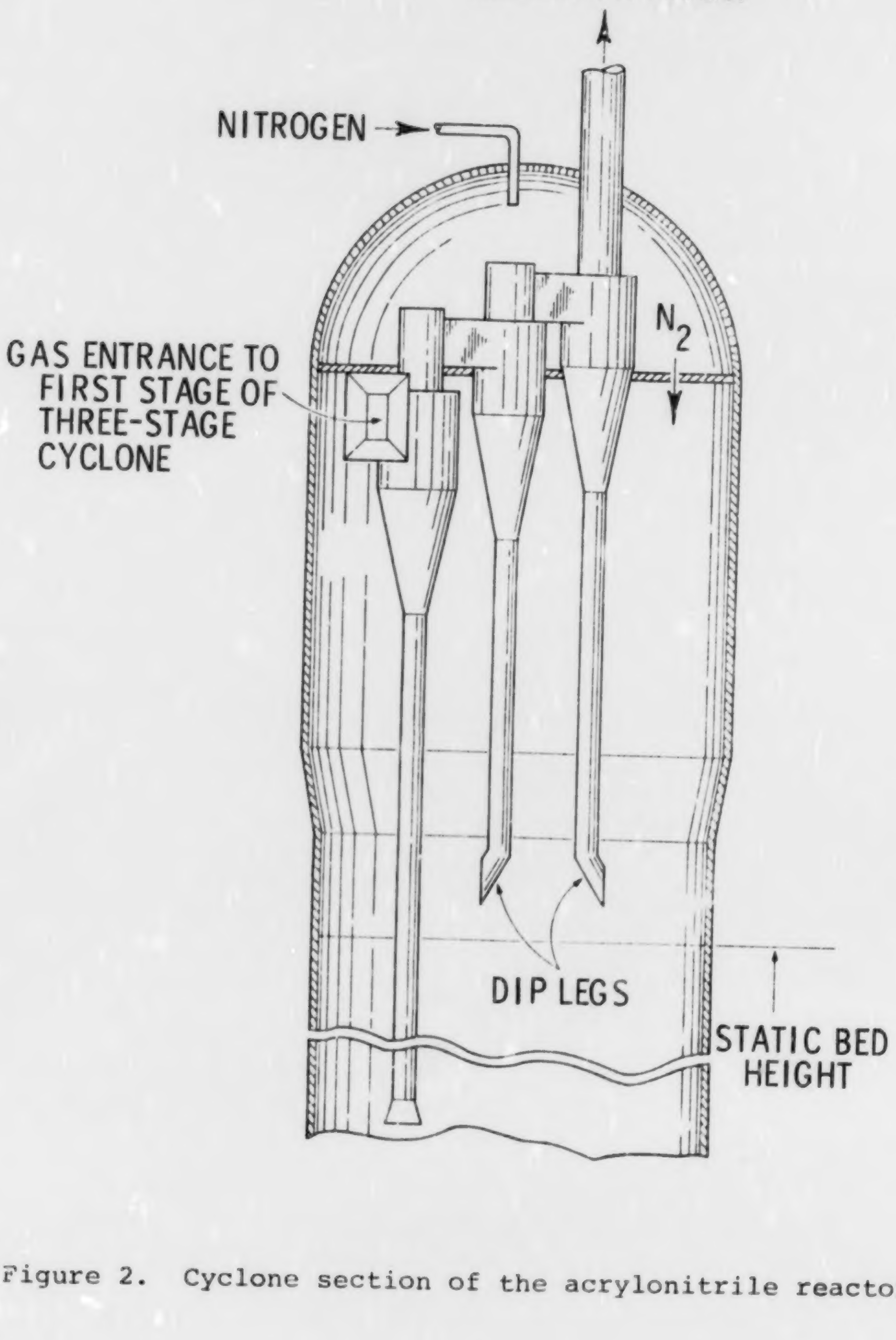
REACTOR EFFLUENT
NITROGEN
N_2
GAS ENTRANCE TO FIRST STAGE OF THREE-STAGE CYCLONE
DIP LEGS
STATIC BED HEIGHT

Figure 2. Cyclone section of the acrylonitrile reactor.[5]

Test data were obtained on a 3.3-m diameter multistage reactor operating at a 0.45 m/s superficial vapor velocity and using the catalyst described in U.S. Patent 3,198,750.[7] Propylene, ammonia, and air (1/1.15/10.5 molar ratio) were reacted at 493°C to 500°C and approximately 219 kPa. When no inert gas was added to the upper compartment, the temperature increased to ∿538°C and the yield declined to 60% to 63%. Deposits were found on reactor internals.[7]

When nitrogen was added to the upper compartment, the temperature remained normal and the yield was 66% to 68% at a 90% to 95% conversion[5] over an extended period. Catalyst loss from the reactor did not exceed 45 kg/day (1.9 g/kg) after stable conditions were achieved.

Using the data supplied in the above patent[7] for the 3.3-m diameter reactor, the annual operating capacities for the operations discussed above were calculated. The capacity at 68.2% yield was 8,400 metric tons/yr and the capacity at 63% yield was 7,800 metric tons/yr assuming an on-stream factor of 90% for 360 days/yr. These capacities were determined in the following manner:

$$\text{Capacity} = (v)\left(\frac{\pi D^2}{4}\right)\left(\frac{P}{RT}\right)(MW)\,(Q')\left(\frac{Y}{100}\right)\left(\frac{3{,}600\ \text{s}}{\text{hr}}\right)\left(\frac{24\ \text{hr}}{\text{day}}\right)\left(\frac{360\ \text{days}}{\text{yr}}\right)(0.9) \qquad (2)$$

where v = superficial velocity, 0.45 m/s
D = reactor diameter, 3.3 m
P = absolute pressure, 219 kPa
T = absolute temperature, 766°K
R = gas law constant, 8.31×10^{-3} (kPa)m^3/(g-mole) K
MW = propylene molecular weight or 42 g propylene/g-mole
Q' = propylene ratio or 1 mole propylene/12.65 moles gas
Y = yield, 68.2% or 63%

The above reactor description is based upon the best information available from the literature. Further details of reactor design are considered proprietary by SOHIO (personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974) and are not available.

b. System Heat Balance--
The ammoxidation of propylene is an exothermic chemical reaction which has a heat release of 17.6 kJ/g acrylonitrile formed. Side reactions which occur in the reactor due to by-product formation and catalyst regeneration also liberate heat. The heat release due to these reactions is ∿4.3 kJ/g acrylonitrile formed. The total heat release for all reactions has been estimated to be 21.93 kJ/g acrylonitrile formed.[3]

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[7] Callahan, J. L. Mixed Antimony Oxide - Uranium Oxide Oxidation Catalyst. U.S. Patent 3,198,750 (to the Standard Oil Company), June 27, 1967.

Reactor temperature control is maintained by internal cooling coils which generate ∿75% of the total process steam requirements. The remainder (∿25%) of the process steam is generated in a waste heat boiler where the product gases are cooled from 510°C to 230°C. The feed material to the waste heat boiler is the reactor product (stream 5). Table 7 shows a typical heat balance for an acrylonitrile plant.

TABLE 7. ACRYLONITRILE REACTOR SYSTEM HEAT BALANCE[a],[3]

Heat out	kJ/g acrylonitrile
Steam generation	
Cooling coils inside reactor	15.66
Waste heat boiler	5.02
Reactor heat losses	0.10
Quench (232°C to 43°C)	9.52
Incremental effluent heat content[b]	-2.33
TOTAL	27.97
Heat in	**kJ/g acrylonitrile**
Exothermic heat of reaction	
Acrylonitrile formation	21.93
Effluent neutralization	3.20
Feed vaporization and preheat	2.84
TOTAL	27.97

[a] Basis: Data shown later in Table 12; feed preheated to 149°C; reactor outlet temperature 510°C (max).

[b] Difference in heat content of reactor product @ 43°C and feed @ 27°C (liquid) plus air @ 38°C.

c. Quencher--
Cooled reactor effluent (stream 6) is sent to a quencher for additional cooling and for ammonia and catalyst fines removal. A SOHIO patent (U.S. 3,468,624[8]) describes the scrubbing of reactor effluent gases with dilute sulfuric acid for the removal of excess ammonia.

The quencher operates at 40°C to 50°C and 135 kPa to 205 kPa. Streams entering the quencher are the cooled reactor effluent (stream 6), sulfuric acid (stream 8), and the wastewater column volatiles (stream 10). Stream 7 is the quenched reactor effluent.

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[8] Miller, A. F., and M. L. Salehar. Process for the Recovery of Ammonium Salts from Waste Streams in an Acrylonitrile Plant. U.S. Patent 3,468,624 (to The Standard Oil Company), September 23, 1969.

Bottoms from the quencher are fed to a wastewater column where the volatile components of this stream are stripped using steam (stream 9). Stream 11 (wastewater column bottoms) is sent to the deep well pond.[9]

The recovery of ammonium sulfate crystals by evaporation of water from the bottoms has been unsuccessful previously because organic material ("heavies") also precipitates and plugs the equipment. The precipitation of the organic material has been prevented by adding ammonium hydroxide and controlling pH to 9.8. After partial evaporation, the solution can be saturated with ammonia to precipitate a 98.3% pure ammonium sulfate salt.[10] Recovery of ammonium sulfate is not currently practiced due to a small market demand for this material.

d. Absorber--
The acrylonitrile product and by-products (hydrogen cyanide and acetonitrile) are recovered in a tray-type absorber tower (personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974) which can be operated either with or without auxiliary cooling. (Personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974.) Operation of the absorber at low temperatures (4°C versus 43°C) increases acrylonitrile recovery. Water, used as the absorption medium, enters the top of the tower. The gas stream entering the bottom of the tower, quenched reactor product (stream 7), is scrubbed to remove acrylonitrile, acetonitrile, and hydrogen cyanide. The absorber vent gas (stream 12) is vented to the atmosphere or sent to a thermal oxidizer or catalytic incinerator.[3]

e. Recovery Column--
The absorber bottoms (stream 14) are sent to a recovery column for separation of crude acrylonitrile (stream 17) and crude acetonitrile stream 16). The crude acrylonitrile stream contains ∿80% acrylonitrile and ∿12% hydrogen cyanide with the balance being water and organics.[9,10] This stream is sent to a storage tank prior to purification.

f. Acetonitrile Column--
The crude acetonitrile (stream 16) is sent to the acetonitrile column. This stream is separated into acetonitrile (stream 20),

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[9] Fitzgibbons, W. O., E. M. Schwerko, and A. H. Brainard. Deep Well Disposal Process for Acrylonitrile Process Wastewater. U.S. Patent 3,734,943 (to The Standard Oil Company), May 22, 1973.

[10] Halvorson, D. O., and S. N. Vines. Anti-Foulant in Acrylonitrile Manufacture. U.S. Patent 3,691,226 (to E. I. du Pont de Nemours and Company), September 12, 1972.

water recycle (stream 15), and acetonitrile column bottoms (stream 19). Acetonitrile is incinerated; the water recycle is returned to the top of the absorber; and the acetonitrile column bottoms are sent to the deep well pond.[9]

3. Product Purification

Product purification is normally used to upgrade crude acrylonitrile to a saleable product. However, one plant currently also produces a saleable acetonitrile product from crude acetonitrile.[3] (Personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974.) Since four of the five operating plants do not produce acetonitrile for sale, discussion of product purification will be limited to acrylonitrile purification.

a. Light Ends Column--

Crude acrylonitrile (stream 17) is fed from tank storage to the light ends column to remove low boiling materials. Two process streams leave the column: (1) light ends column bottoms (stream 23); and (2) hydrogen cyanide (stream 21). The light ends column bottoms are sent to the product column while the hydrogen cyanide is incinerated or sold as a by-product.

b. Product Column--

Light ends column bottoms (stream 23) are fed to the product column. Streams leaving this column consist of product acrylonitrile (stream 24) and product column bottoms or heavy ends (stream 25). The product acrylonitrile stream is 99+% pure while the heavy ends stream contains organic polymers, water, hydrogen cyanide, and miscellaneous organics.

4. Wastes Disposal

Wastes generated within an acrylonitrile plant consist of gaseous wastes (including those discussed in Section IV), liquid wastes (wastewater column bottoms, acetonitrile column bottoms, heavy ends, crude acetonitrile, and hydrogen cyanide), and solid wastes (catalyst fines and organic polymers). These wastes are disposed of using deep well injection for some liquid wastes, a settling pond for solid wastes, and incineration for the remaining liquid and gaseous wastes. The following equipment is used for wastes disposal: (1) deep well pond (settling pond) with deep well injection, (2) flare, and (3) thermal oxidizer (incinerator).[3]

a. Deep Well Pond and Deep Well Injection--

Wastewater generated within the acrylonitrile plants contains ammonium sulfate, catalyst fines, organic polymers, and miscellaneous organic materials. Sources of wastewater include wastewater column bottoms and acetonitrile column bottoms as described previously.

The two wastewater streams generated in the plant (streams 11 and 19) are mixed and sent to a deep well pond (stream 13). The composition of these two streams are given in Tables 8 and 9 as reported in Reference 9.

TABLE 8. COMPOSITION OF WASTEWATER COLUMN BOTTOMS[9]

Component	Concentration, wt %
Water	85.1
Ammonium sulfate	8.1
Acrolein-$(NH_4)_2SO_4$ reaction product	0.4
Heavy organic material	6.1
Acrylonitrile	0.02
Acetonitrile	0.3
Maleonitrile	0.2
Fumaronitrile	0.08

TABLE 9. COMPOSITION OF ACETONITRILE COLUMN BOTTOMS[9]

Component	Concentration, wt %
Water	98.2
Ammonium sulfate	0.02
Heavy organic material	1.74

The acrylonitrile plant wastewater (stream 13) has the appearance of strong tea or coffee.[8] Table 10 shows the composition of acrylonitrile plant wastewater as reported by Reference 11 and a personal communication with Arthur W. Busch, Regional Administrator, Region IV, U.S. Environmental Protection Agency, February 1974.

These liquids (stream 13) are sent to a deep well pond for separation of solids from the water. The pond typically is 60 m by 90 m in size and may be uncovered or covered with a layer of lube oil. Heavy oil is used to limit emission of hydrocarbon vapors from the pond surface. Runoff from the settling pond is disposed of using deep well injection. Solids collected from the deep well pond are disposed by a regulated, EPA-approved, landfill operator.[3]

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[11] Train, R. E. Development Document for Interim Final Effluent Limitations and New Source Performance Standards for the Significant Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category. EPA-400/1-75/045, U.S. Environmental Protection Agency, Washington, D.C., November 1975. 391 pp.

TABLE 10. ACRYLONITRILE PLANT WASTEWATER[a,11]

Material discharged	Concentration, mg/l	Effluent factor, g/kg
Raw wastewater	–[b]	4,470
Biological oxygen demand	8,620	38.7
Chemical oxygen demand	32,800	133
Total organic carbon	14,400	57.5
Total solids	36,700 to 57,800	163 to 182
Total suspended solids	184 to 630	0.915 to 1.78
Total dissolved solids	36,500 to 57,200	161 to 181
Oil and grease	135 to 168	0.475 to 0.657
Total nitrogen (as N_2)	4,040 to 22,000	16.9 to 62.1
Ammonia nitrogen (as N_2)	2,600 to 13,600	10.3 to 38.3
Nitrile nitrogen (as N_2)	197 to 270	0.755 to 0.97
Phosphate	0.152 to 6.15	0.0004 to 0.0298
Phenol	0.165 to 2.28	0.0007 to 0.0064
Sulfate	2,700 to 5,309	64.1 to 74.3
Zinc	0.052 to 2.1	0.00002 to 0.0092
Chloride	125 to 858	0.616 to 2.42
Iron	3.13 to 4.24	0.0088 to 0.0182
Copper	≤0.5	≤0.00024
Chromium	≤0.05	≤0.00014
Cadmium	≤0.05	≤0.00024

Other compounds which have been qualitatively identified include:[a]

- Acetaldehyde
- Acrolein
- Hydrogen cyanide
- Acetic acid
- Fumaronitrile
- Acrylic acid
- Acrylamide
- Acrylonitrile
- Acetonitrile
- Maleonitrile
- Organic polymers
- Propionitrile
- Ammonium formate
- Methacrylonitrile
- trans-Crotonitrile
- cis-Crotonitrile
- Allyl cyanide
- Benzonitrile
- Nicotinonitrile
- Malononitrile
- Furonitrile
- Ticoline
- Lutidine compounds
- Benzene
- Toluene
- Ammonium acetate
- Ammonium methacrylate
- Ammonium acrylate
- Succinonitrile
- Acetone
- Acetaldehyde cyanohydrin
- Acetone cyanohydrin
- Acrolein cyanohydrin
- Pyrazole
- Methyl pyrazine
- Cyanopyrazine
- Pyrazine

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[a] Personal communication, A. W. Busch, Regional Administrator, Region IV, U.S. Environmental Protection Agency, February 1974.

[b] Not applicable.

b. Flare--
The process flare, using a natural gas pilot flame, is fed by purge vents from the recovery column (stream 18), light ends column (stream 22), and the product column (stream 26). During absorber upsets, flaring of propylene occurs. These periods last for less than 5 minutes. Steam is continuously supplied to the tip of the flare and the quantity is varied as needed to control smoke formation.[3]

During plant upset or other emergencies, the following streams are diverted to the flare:[3]

- Propylene Storage - Tank relief valves discharge to the flare when the storage temperature exceeds the design storage temperature (usually 38°C).[3]

- Propylene Feed - Propylene is vented to the flare if the source of heat for feed vaporization is lost and freezeup of the vaporizer occurs (about once every 2 years, with the venting lasting about 2 hours with propylene loss ∿0.35 kg/kg of acrylonitrile). In addition, the venting of vaporizers to the flare during scheduled annual shutdown results in venting propylene (∿0.09 g/kg).[3]

c. Incinerator--
By-product acetonitrile and hydrogen cyanide are incinerated in a thermal oxidizer. A description of this unit is given in Section IV.

5. Product Storage and Transportation

The tankage requirements for a 140,000-metric ton acrylonitrile plant are summarized in Table 11 (personal communication, A. F. Pier of Monsanto Company and L. B. Evans of the U.S. Environmental Protection Agency, June 19, 1972). Fixed roof storage tanks are used to store acrylonitrile product (in run-down tanks and long-term storage), off-specification acrylonitrile, crude acrylonitrile (in surge tanks used to store feed to product purification section of plant), and crude acetonitrile (in surge tanks used to store acetonitrile prior to incineration).

Acrylonitrile is transported to the customer by one of four methods: railroad tank car, tanker truck, barge, or 0.21-m^3 (55-gal) drums. Acrylonitrile is loaded on railroad tank cars and tanker trucks by means of loading racks.[12]

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[12] Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

TABLE 11. TANKAGE REQUIREMENTS FOR A 121,500-METRIC TON/YR ACRYLONITRILE PLANT[a,b]

Stored material	Capacity, m^3	Turnovers per yr	Vent height, m
Acrylonitrile	114	450	15.2
Acrylonitrile	114	450	15.2
Acrylonitrile	1,700	25	15.2
Acrylonitrile	1,700	25	15.2
Acrylonitrile	1,700	25	15.2
Off-specification acrylonitrile	473	5	15.2
Crude acrylonitrile	871	2	15.2
Crude acrylonitrile	871	2	15.2

[a] All tanks use conservation vents.

[b] Personal communication, A. F. Pier of Monsanto Company and L. B. Evans of the U.S. Environmental Protection Agency, June 19, 1972.

Loading racks contain equipment to meter and deliver products into tank vehicles from storage either by overhead filling through the top hatch in the tank vehicle or by bottom filling at ground level. The elevated platform structure employed for overhead filling, constructed with hinged side platforms attached to the sides of a central walkway, can be raised when not in use. For loading, a tank vehicle is positioned adjacent to the central walkway and a hinged side platform is lowered to rest upon the top of the tank vehicle to access the top hatch. The meters, values, loading tubes or spouts, motor switches, and similar necessary loading equipment are located on the central walkway. Bottom loading facilities are simpler since the tank vehicle is easily filled through accessible fittings on its underside.

Acrylonitrile is loaded on barges at modern terminals by equipment similar to that used for elevated tank vehicle loading except for size. A pipeline manifold with flexible hoses is used for loading at older terminals. Marine installations are considerably larger and operate at much greater loading rates than inland loading facilities.

The loading arm assembly refers to the equipment at the discharge end of a product pipeline that is necessary for filling tank vehicles. Component parts include piping, valves, meters, swivel joints, fill spouts, and vapor collection adaptors.

Overhead loading arms can be pneumatic, counterweighted, or tension spring depending upon the manner in which the vertical movement of the arm is achieved. Bottom loading employs a flexible hose or a nonflexible, swing-type arm connected to the vehicle from the ground level storage facility.

Loading arms at modern marine terminals are similar in design to those used for overhead loading of tank vehicles. The barge loading arms are too large for manual operation, requiring a hydraulic system to effect arm motion. Older installations use reinforced flexible hoses to convey products from pipeline discharge manifolds to the barge. The hoses are positioned by means of a winch or crane.

6. Plant Shutdown, Turnaround, and Startup

Each acrylonitrile plant schedules shutdowns, turnarounds, and startups for each major piece of processing equipment (reactors, absorber, fractionation columns, and storage tanks) to permit the necessary vessel and tank maintenance.[3]

Acrylonitrile reactors are shut down frequently. Plants contain two to six reactors and each reactor undergoes shutdown, turnaround, and startup on an average of four times per year. Each reactor startup lasts about 1 hour, during which time effluent from the reactor bypasses the absorber and is discharged directly to the atmosphere. The gases discharged consist of natural gas combustion products.[3]

Other processing equipment normally undergoes shutdown, turnaround, and startup once every 12 to 14 months. Prior to entry by plant personnel, the equipment is purged of hazardous liquids and gases. Hydrocarbon vapors contained in the purge gas are incinerated to control hydrocarbon emissions.[3]

B. PLANT MATERIAL BALANCE

Figure 1, presented earlier, shows the flow diagram for a representative acrylonitrile plant. Table 12 contains a material balance for such a plant.

Sources of atmospheric emissions from acrylonitrile plants are: absorber vent (stream 12), incinerator stack (stream 29), flare stack (stream 27), deep well pond (stream 30), product and byproduct storage (stream 31), transport loading facility (stream 32), and fugitive emissions (stream 28).

C. PLANT LOCATIONS

Four companies manufacture acrylonitrile at six locations in the U.S. Table 13 lists the manufacturers and plant capacities. Figure 3 shows the plant locations. The number of processing units (individual plants) at each location is also given in Table 13. The population densities in the counties surrounding the plants were calculated by dividing the county population by the county area for the 1970 census. For those cases where a plant was

TABLE 12. MATERIAL BALANCE FOR A REPRESENTATIVE ACRYLONITRILE PLANT[a]

	Stream number									
	1	2	3	4	5	6	7	8	11	12
	Description									
Component	Propylene feed	Ammonia feed	Process air	Reactor feed	Reactor product	Cooled reactor product	Quenched reactor product	Sulfuric acid	Wastewater column bottoms	Absorber vent gas[b]
Nitrogen		2.5[c]	5,865[d]	5,867	5,867	5,867	5,867			5,867[d]
Oxygen			1,561	1,561	103	103	103			103
Carbon dioxide					185	185	185			185
Water			83.5	83.5	1,653	1,653	1,653		3,470	922
Propylene	1,289			1,289	32[e]	32	32			32
Propane	22			22	22[e]	22	22			22
Ammonia		553.1		553.1	24	24				
Carbon monoxide					178	178	178			178
Acrylonitrile					1,000[e]	1,000	1,000			<0.1
Acetonitrile					118[e]	118	118			0.6
Hydrogen cyanide					118[e]	118	118		0.9	0.3
Sulfuric acid								70.6		
Ammonium sulfate									93.2	
Oxygenated hydrocarbons					95	95			79.3	
Organic polymers										
TOTALS	1,311	556	7,510	9,375	9,395	9,395	9,276	70.6	3,643	7,310

(continued)

Note: Blanks indicate no component present in stream.

[a] All values are g/kg of product acrylonitrile.

[b] Emissions determined through field sampling.

[c] Ammonia used is agricultural grade as described in Section III.A.1.

[d] Composition of the combined reactor feed is based upon the following mole rates: 1 C_3H_6/1.06 NH_3/8.4 air.

[e] Conversion of propylene = 98%; conversion of propane = 0%; yield of acrylonitrile is 0.78 g AN/g C_3H_6; yield of HCN and ACN = 0.09 g/g C_3H_6.

TABLE 12 (continued)

Component	Stream number 13	14	15	16	17	19	20	21	23	24
	Description Acrylonitrile plant wastewater	Absorber bottoms	Water recycle	Crude acetonitrile	Crude acrylonitrile	Acetonitrile column bottoms	Acetonitrile	Hydrogen cyanide	Light ends column bottoms	Product acrylonitrile
Nitrogen										
Oxygen										
Carbon dioxide										
Water	4,470	23,714	23,000	23,000	10,000	1,000				
Propylene										
Propane										
Ammonia										
Carbon monoxide										
Acrylonitrile		1,000			1,000				1,000	1,000
Acetonitrile		118		118			118		5.1	3.1
Hydrogen cyanide	1.0	118			118			118		
Sulfuric acid										
Ammonium sulfate	93									
Hydrocarbons	79	16		17.5	1.2	7.5			1.0	1
Organic polymers					7				7.1	1
TOTALS	4,643	24,966	23,000	23,136	11,126	1,008	118	118	1,013	1,005

(continued)

TABLE 12 (continued)

	Stream number						
	25	27	28	29	30	31	32
	Description						
Component	Heavy ends	Flare stack gas	Fugitive losses	Incinerator stack gas	Deep well pond emissions	Storage tank losses	Product transport loading facility vent
Nitrogen		72.5		1,771			
Oxygen		2		174			
Carbon dioxide		16		300			
Water		8		435			
Propylene		0.02	0.006				
Propane			0.0006				
Ammonia			0.006				
Carbon monoxide							
Acrylonitrile		0.04	0.4			0.802	
Acetonitrile	2		0.02				
Hydrogen cyanide		0.35		0.034		0.81	0.0065
Sulfuric acid							
Ammonium sulfate							
Hydrocarbons					7		
Organic polymers	6.1						
TOTALS	8.1	98.9	0.43	2,680	7	0.81	0.0065

TABLE 13. ACRYLONITRILE PLANTS[13,14]

Company	Location	Capacity, metric tons/yr	Number of process units	County population density, persons/km^2
American Cyanamid Co.	New Orleans, LA	91,000	1	1,103
Du Pont Co.	Beaumont, TX	160,000	1	98
Du Pont Co.	Memphis, TN	130,000	1	371
Monsanto Co.	Alvin, TX	200,000	2	29
Monsanto Co.	Texas City, TX	190,000	2	29
Vistron Corp.	Lima, OH	91,000[a]	1	104
TOTALS		862,000	8	

[a] Personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation. October 3, 1974.

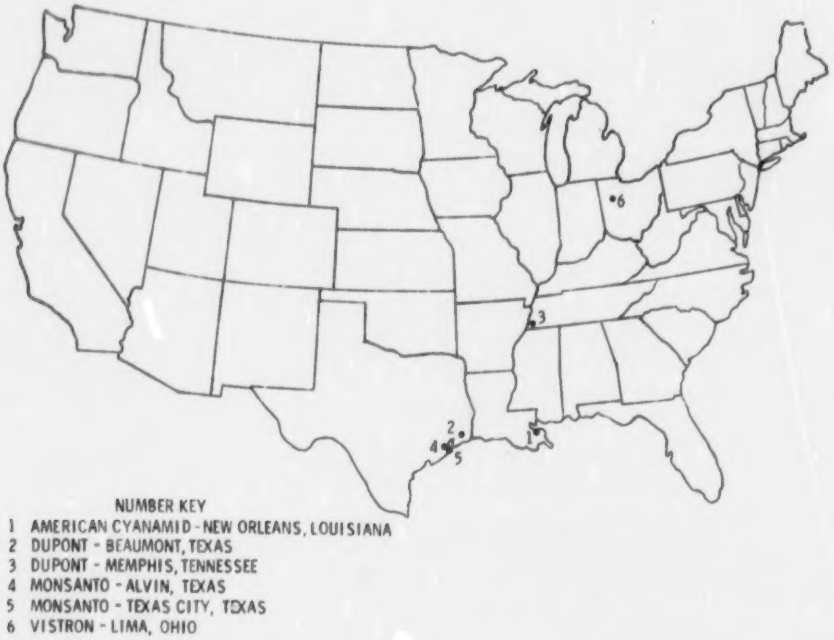
1
2
3
4
5
6
NUMBER KEY
1 AMERICAN CYANAMID - NEW ORLEANS, LOUISIANA
2 DUPONT - BEAUMONT, TEXAS
3 DUPONT - MEMPHIS, TENNESSEE
4 MONSANTO - ALVIN, TEXAS
5 MONSANTO - TEXAS CITY, TEXAS
6 VISTRON - LIMA, OHIO

Figure 3. Locations of acrylonitrile manufacturing plants.

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[13] Chemical Profile: Acrylonitrile. Chemical Marketing Reporter, 211(2):9, January 10, 1977.

[14] Statistical Abstract of the United States, 1974, 95th Edition. U.S. Department of Commerce, Bureau of the Census, Washington, D.C., 1974. pp. 445-461.

located on a county line, a weighted average was used for the population density.

The representative plant capacity based on the number of locations is 140,000 ± 50,000 metric tons/yr, while the representative plant capacity based on the number of processing units is 110,000 ± 20,000 metric tons/yr. The value based on plant locations (140,000 ± 50,000 metric tons/yr) is used in Section V to define the representative plant capacity.

SECTION IV

EMISSIONS

A. SELECTED POLLUTANTS

1. Locations and Description of Emissions

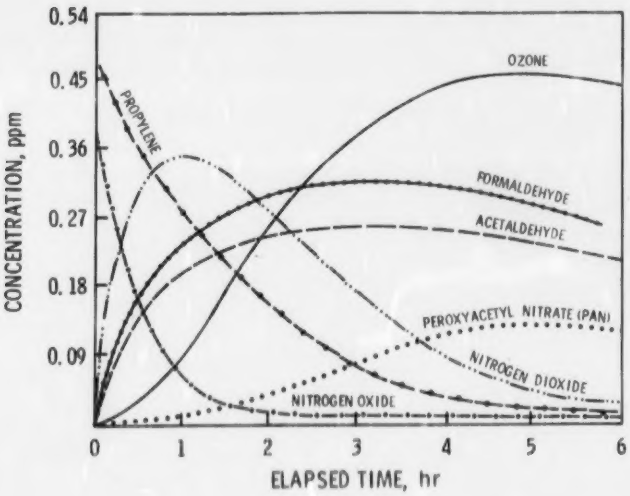
The process mechanism and the formation of atmospheric emissions were described in Section III. Based on that information, the emission points within an acrylonitrile plant are the absorber vent, incinerator, flare, deep well pond, storage tanks, product transport loading facility, and fugitive emission points. Criteria pollutants which are emitted include carbon monoxide, hydrocarbons, nitrogen oxides, and sulfur oxides.[3] A total of 43 chemical substances were identified as potential emissions from acrylonitrile plants and these are presented in Table 14. This list was compiled from two analyses of quencher wastewater;[11] from a personal communication with A. W. Busch, Regional Administrator, Region IV, U.S. Environmental Protection Agency, February 1974; and from atmospheric emissions identified by Schwartz et al.[3] A sampling program was performed to quantify these compounds plus others which may not previously have been known to be present.

TABLE 14. SUSPECTED EMISSIONS FROM ACRYLONITRILE MANUFACTURE PRIOR TO FIELD SAMPLING[a,b,3,11]

Acetaldehyde
Acetaldehyde cyanohydrin
Acetic acid
Acetone
Acetone cyanohydrin
Acetonitrile
Acrolein
Acrolein cyanohydrin
Acrylonitirle
Allyl cyanide
Ammonium acetate
Ammonium acrylate
Ammonium formate
Ammonium methacrylate
Benzene
Benzonitrile
Carbon monoxide
cis-Crotonitrile
Cyanopyrazine
Ethane
Ethylene
Fumaronitrile
Furonitrile
Hydrogen cyanide
Lutidine compounds
Maleonitrile
Malononitrile
Methacrylonitrile
Methane
Methyl pyrazine
Nicotinonitrile
Nitrogen oxides
Propane
Propionitrile
Propylene
Pyrazine
Pyrazole
Succinonitrile
Sulfur dioxide
Sulfur trioxide
Ticoline
Toluene
trans-Crotonitrile

[a] Personal communication, A. W. Busch, Regional Administrator, Region IV, U.S. Environmental Protection Agency, February 1974.
[b] Acrylonitrile and benzene are suspected carcinogens.

Table 15 lists the materials found in atmospheric emissions from acrylonitrile plants together with the threshold limit values (TLV's®) of the forms emitted,[15] their primary ambient air quality standards where applicable,[16] their health effects,[1] and their atmospheric stabilities. Hydrocarbon emissions from acrylonitrile manufacture can contribute to the formation of photochemical smog. Figure 4 shows the products formed upon photo-oxidation of propylene,[17] the hydrocarbon that is emitted in the largest quantities.



INITIAL CONDITIONS:
PROPYLENE CONCENTRATION = 0.54 ppm
NITROGEN OXIDE CONCENTRATION = 0.40 ppm

Figure 4. Products of photochemical oxidation of propylene.[17]

2. Factors Affecting Emissions

a. Absorber Vent Gas--

The absorber vent gas consists of reactor product which has been cooled, neutralized, and scrubbed for nitrile recovery. Absorber vent gas composition depends on catalyst type, reactor operating

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[15] TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 97 pp.

[16] Air Quality Data - 1973 Annual Statistics. EPA-450/2-74-015, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1974. 151 pp.

[17] Pitts, J. N., A. C. Lloyd, and J. L. Sprung. Ecology, Energy, and Economics Chemistry in Britain, 11;247-256, July 1975.

TABLE 15. CHARACTERISTICS OF MEASURED EMISSIONS FROM ACRYLONITRILE MANUFACTURE

Material emitted	TLV,[15] g/m^3	Primary ambient air quality standard,[16] g/m^3		Health effects[1]	Atmospheric stability
Carbon monoxide	0.055	0.040	(1 hr)	Asphyxiant; combines with hemoglobin to prevent dissociation of oxyhemoglobin	Stable
Hydrocarbons (nonmethane)		0.000160[a]	(3 hr)		Contributes to photochemical smog
Nitrogen oxides (as NO_2)	0.009	0.000100	(1 yr)	Toxic	Contributes to photochemical smog
Sulfur oxides (as SO_2)	0.013	0.000365	(24 hr)	Strong irritant to eyes and mucous membranes	Forms sulfuric acid and sulfates
Methane	0.714			Simple asphyxiant	
Ethane	1.34			Simple asphyxiant	
Ethylene	1.25			Simple asphyxiant	
Propane	1.96			Simple asphyxiant	
Propylene				Simple asphyxiant	
Butene				Simple asphyxiant	
Butanes	2.59			Simple asphyxiant	
Acetaldehyde	0.18			Moderately toxic and narcotic	
Pentanes	1.8			Asphyxiant	
Methanol	0.260			Toxic by ingestion	
Hexanes	0.360			Moderately toxic by inhalation	
Benzene	0.03			Toxic by ingestion, inhalation, skin absorption; suspected carcinogen	
Toluene	0.375			Toxic by ingestion, inhalation, skin absorption	
Acrylonitrile	0.045			Toxic by inhalation and skin absorption	
Ethanol	1.90			Noncumulative poison	
Acetonitrile	0.070			Toxic	
Hydrogen cyanide	0.011			Toxic by ingestion, inhalation, skin absorption	
Fumaronitrile					
Pyridine	0.015			Toxic by ingestion and inhalation	
Propionaldehyde				Toxic and irritant	
Furan				Toxic by skin absorption	
Ammonia	0.018			Toxic and irritant	
Allyl alcohol	0.005			Toxic by ingestion and inhalation, strong irritant to eyes and skin	

Note: Blanks indicate data not available.

[a] There is no primary ambient air quality standard for hydrocarbons; the value used in this report for hydrocarbon is a guideline for meeting the primary ambient air quality standard for oxidants.

conditions, absorber temperature, reactor feed rates and feed material composition.[3]

Catalyst types used in the manufacture of acrylonitrile include Catalyst A (prior to 1967), Catalyst 21 (1967 to 1973), and Catalyst 41 (since 1973). All plants used Catalyst 41 in 1976. Emission factors for four plants using Catalyst 21 are presented in Table 16 which shows the variability of emissions due to the factors affecting emissions when using Catalyst 21. The average emission factors for Catalyst 21 and Catalyst 41 are compared in Table 17. This table shows the reduction in absorber vent emissions, by chemical substance, caused by the change in catalyst type. Emission factors for nitrogen indicate an increase of 21% in rated capacity of existing plants due to the change to Catalyst 41. The calculation of this increased capacity is given in Appendix A together with field sampling data for absorber vent emissions.

b. Incinerator Stack Gas--

Acrylonitrile plants use an incinerator (thermal oxidizer) for the ultimate disposal of some liquid wastes and residues. Materials incinerated can include acetonitrile by-product, hydrogen cyanide by-product, polymers and heavy ends from still bottoms, and quencher wastewater. Normally, only the acetonitrile and hydrogen cyanide are incinerated since the polymers, heavy ends, and wastewater are disposed of in deep wells. During deep well injection pump failure, which occurs on the average of once a year, these wastes are also incinerated.[3]

The amounts of acetonitrile and hydrogen cyanide by-products incinerated are determined by their market demand. Excess by-product formed is incinerated. Currently (1976), only one plant (Vistron Corporation, Lima, Ohio) markets acetonitrile (personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974). However, Du Pont has announced plans to market by-product acetonitrile which is to be recovered and refined at its Beaumont, Texas plant. Should the market for acetonitrile expand as anticipated, Du Pont's Memphis, Tennessee plant could provide additional acetonitrile.[18] Each of the plants markets hydrogen cyanide. Fifty percent of the hydrogen cyanide is sold, while 40% is incinerated and 10% is sent to deep well disposal.[3]

Four plants surveyed by Houdry dispose of quencher wastewater by steam stripping volatile organics from the water in a wastewater column and sending the water to a deep well.[3]

Besides requiring more fuel, incinerating the quencher wastewater increases atmospheric emissions. Sulfuric acid in the quencher

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[18] Acetonitrile's Economics are Alluring to Du Pont. Chemical Marketing Reporter, 208(16):4, October 1975.

TABLE 16. ABSORBER VENT DISCHARGES USING CATALYST 21[3]

Material emitted	Emission factor by plant, g/kg 51-1	51-2	51-3	51-4	Mean ± 95% confidence limit
Carbon dioxide	294	508	450	350	400 ± 153
Carbon monoxide	180	178	187	167	178 ± 13.2
Methane			1		1
Ethane and ethylene			8	1	4
Propylene	47	52	50	50	50 ± 3.3
Propane	124	144	35	35	84.5 + 91.9 - 84.5
Hydrogen cyanide	2	0.5		4	2 ± 4
Acrylonitrile	29	0.4	6	9	11 ± 20
Acetonitrile	6	8			7
Acetaldehyde				0.2	0.2
Acetone				0.13	0.13
Acrolein				0.08	0.08
Nitrogen	9,726	7,222	9,133	8,774	8,714 ± 1,701
Oxygen	865	303	856	763	697 ± 424
Water	605		383	787	592 + 1,470 - 592

Note: Blanks indicate data not available.

TABLE 17. EFFECT OF CATALYST TYPE ON ACRYLONITRILE ABSORBER VENT EMISSIONS[a]

Component	Emission factor, g/kg Catalyst 21	Catalyst 41	Percent reduction in emission factor by use of Catalyst 41
Nitrogen	8,714	5,865	32.7
Oxygen	697	206	70.4
Carbon dioxide	400	185	53.8
Carbon monoxide	178	79.3	55.5
C_3-Hydrocarbons	134	55.0	59
Acrylonitrile	11	0.039	99.6
Acetonitrile	7	0.625	91.2
Hydrogen cyanide	2	0.275	86.2

[a] Catalyst 21 is no longer used by any operating plant. Purpose of the table is to show the reduction in emissions since the catalyst change.

water, used for neutralization of reactor effluents, forms ammonium sulfate. The amount of ammonium sulfate in the wastewater, which represents 0.093 kg/kg of acrylonitrile product, forms 0.044 kg/kg of sulfur oxides (as SO_2) if incinerated.

Emission factors for the incineration of all by-product acetonitrile and 40% of the hydrogen cyanide by-product are given in Tables 18 and 19. The values in Table 18 show the plant data using Catalyst 21 obtained by Schwartz et al.,[3] while Table 19 shows the emissions data using Catalyst 41 obtained through field sampling. Composited field sampling results for two incinerators are shown in Appendix B.

TABLE 18. REPORTED INCINERATOR STACK EMISSION FACTORS[3]
(Catalyst 21)

Material emitted	Emission factor by plant, g/kg				Mean value, g/kg
	51-1	51-2	51-3	51-4	
Nitrogen	–[a]	1,251	–[a]	2,290	1,771
Oxygen	–[b]	174	–[a]	–[b]	174
Carbon dioxide	–[a]	282	–[a]	317	300
Water	–[b]	160	–[a]	709	435
Nitrogen oxides	7.3	0.01	–[b]	0.4	2.6
Sulfur oxides	–[c]	–[c]	26	–[c]	6.5
Ammonia	0.3	–[b]	–[b]	–[b]	–[d]
Hydrogen cyanide	0.02	0.001	–[b]	–[b]	0.011

[a] Material was qualitatively identified but not quantified.

[b] Not reported.

[c] Values not reported but assumed to be zero.

[d] Representative plant does not incinerate ammonia in 1976, hence, no ammonia emission; i.e., emission factor for ammonia is zero.

TABLE 19. INCINERATOR STACK EMISSION FACTORS FROM FIELD SAMPLING
(Catalyst 41)

Material emitted	Emission factor, g/kg
Carbon monoxide	0.0040 ± 10%
Hydrocarbons	0.0203 ± 50%
Nitrogen oxides	0.5420 ± 23%
Sulfur oxides	0.0176 ± 49%
Methane	0.0023 ± 50%
Acrylonitrile	<0.0015
Acetonitrile	<0.0015
Hydrogen cyanide	0.343 + 428% – 100%

NO_x formation in the incinerator from nitrile (-CN) combustion is 1% to 3% of theoretical based on data for a commercial incinerator presented by Walker.[19] Field sampling shows that 0.6% of the nitrile feed to the incinerator forms nitrogen oxides, and >99% of the nitriles combusted form carbon dioxide and nitrogen.

c. Deep Well Pond--
Acrylonitrile plants use a pond for temporary disposal of plant wastewater. Composition of the wastewater was shown earlier (Section III.A.2.c). This nonaerated pond is used for solids removal from the wastewater prior to deep well injection of the wastewater for ultimate disposal. Since the water contains volatile organic materials, it is a source of atmospheric emissions of hydrocarbons. Reduction in total hydrocarbon emissions can be achieved by covering the pond with a high molecular weight oil. Emission factors obtained through field sampling for controlled and uncontrolled deep well pond emissions are presented in Table 20. The three plants in Texas use a lube oil cover on the pond. Other plants do not.

d. Flare Stack--
A flare is used to burn gaseous hydrocarbon streams. For acrylonitrile plants, the flow rate from the flare is 98.5 g/kg which corresponds to 1,500 kg/hr for the representative plant. Combustion efficiency for flares has been reported as 90% for carbon monoxide and 75% to 80% for hydrocarbons.[20] Atmospheric emission factors given by Schwartz et al.[3] are presented in Table 21.

Feed streams to the flare stack consist of continuous vent streams from decanters used on product purification columns (stripper, extractive distillation, and light ends) and from intermittent streams. The intermittent streams come from emergency use of propylene storage tank pressure relief valves and relief valves on the propylene preheater, and they also result during plant shutdown for equipment purging. The total amount of flare feed during infrequent intermittent releases to the flare is 440 g/kg with 80% coming from the propylene preheater and 20% from plant shutdown purges.[3]

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[19] Walker, H. M. NO_x Formation During Incineration of Nitrogenous Residues. In: Clean Up of Plant Waste Streams, Conference on the Clean Up of Plant Waste Streams, New Orleans, Louisiana, March 12, 1973. 13 pp.

[20] Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry. Volume I: Carbon Black Manufacturing by the Furnace Process. EPA-450/3-73-006-a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1974. 116 pp.

TABLE 20. HYDROCARBON EMISSION FACTORS FOR ACRYLONITRILE DEEP WELL PONDS[a,b] (g/kg)

Component	Uncontrolled[c]	Controlled[d]	Percent reduction from use of control
Pyridine	5.2 ± 74%	0	~100
Fumaronitrile	0.036	0	~100
Methanol	0	0.2 + 138% – 100%	0
Acetaldehyde	0	0.06 + 423% – 100%	0
Ethanol	0	0.1 + 315% – 100%	0
Butanes	0	0.06 + 182% – 100%	0
Pentane	0	0.04 + 172% – 100%	0
Hexanes	0	0.04 + 145% – 100%	0
Benzene	0	0.1 + 150% – 100%	0
Toluene	0	0.02 + 222% – 100%	0
Others, unidentified	7.8 ± 75%	0	~100
Total hydrocarbons	13 ± 61%	1.1 + 117% – 100%	92

[a] Deep well ponds may be used sometimes to treat wastewater generated at other chemical operations adjacent to acrylonitrile plants.

[b] Values shown represent mean values obtained at each plant, ± error as determined by the "Student t" distribution.

[c] An uncontrolled deep well pond measures 60 m by 90 m and does not have any covering over the water surface.

[d] A controlled deep well pond measures 60 m by 90 m and is covered with a 0.1-m layer of lube oil having an average molecular weight of ~500 g/g-mole.

TABLE 21. FLARE STACK EMISSION FACTORS[3] (g/kg)

Component	Plant 51-1	Plant 51-2	Plant 51-3	Plant 51-4	Mean	Standard deviation	Percent error
Total flow	43	105	156	90	98.5	46.55	75
Nitrogen	–[a]	78	–[a]	67	72.5	7.78	96
Oxygen	–[a]	2	–[a]	–[b]	2	0	0
Carbon dioxide	–[a]	14	–[a]	18	16	2.83	+158 -100
Water	–[a]	11	–[a]	5	8	4.24	+476 -100
Nitrogen oxides	–[b]	–[c]	–[b]	0.01	0.01	–[d]	–[d]

[a] Identified by plant, but only qualitatively. [b] Not reported.

[c] Trace. [d] Not applicable.

3. Emission Factors

Emission factors for uncontrolled and controlled emissions from acrylonitrile manufacture are summarized in Tables 22 and 23 for each emission (criteria pollutants and chemical substances) from each emission point. In three of the six acrylonitrile plants, the absorber vent and the deep well pond are controlled. All other emission points are uncontrolled in acrylonitrile plants. Numbers presented represent mean values of the emission factors and their corresponding uncertainties. Data used to generate these tables are taken from Appendixes A through G.

B. DEFINITION OF A REPRESENTATIVE SOURCE

In order to determine the source severity which is described in Section IV.C, a representative source of acrylonitrile manufacture was defined as using the SOHIO ammoxidation of propylene technology and Catalyst 41, and as having an acrylonitrile production capacity of 140,000 metric tons/yr. The representative source has an absorber stack height of 62.79 m, and incinerator stack height of 33.45 m, and a flare stack height of 62.87 m. The representative plant is located in a community with a population density of 402 persons/km^2, 1 km from its nearest community neighbor. Average wind speed at the representative plant is 4.47 m/s. Data used to determine the representative plant are presented in Table 24.

C. SOURCE SEVERITY

To assess the environmental impact of atmospheric emissions from acrylonitrile manufacture, the source severity for each material emitted from each emission point was estimated. Source severity is defined as the pollutant concentration to which the population may be exposed divided by an "acceptable concentration". The exposure concentration is the time-averaged maximum ground level concentration as determined by Gaussian plume dispersion methodology. The "acceptable concentration" is that pollutant concentration at which an incipient adverse health effect is assumed to occur. For criteria pollutants, it is the corresponding primary ambient air quality standard. For noncriteria pollutants, it is a surrogate air quality standard as determined by reducing TLV's for chemical substances using an appropriate safety factor. The source severity, S, is:

$$S = \frac{\overline{\chi}_{max}}{F} \qquad (3)$$

$\overline{\chi}_{max}$ is the time-averaged maximum ground level concentration of each material emitted from a representative plant. F is defined as a primary ambient air quality standard for criteria pollutants (particulate, SO_x, NO_x, CO, and hydrocarbons), while for noncriteria pollutants,

$$F \equiv TLV \cdot 8/24 \cdot 0.01,\ g/m^3 \qquad (4)$$

TABLE 22. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (UNCONTROLLED EMISSIONS)
(g/kg)

	Emission point						Storage tank emission point				
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Two product acrylonitrile run-down tanks[b]	Three product acrylonitrile field storage tanks[b]	Off-specification acrylonitrile	Two crude acrylonitrile storage tanks[b]	Total
Pollutants											
Carbon monoxide	79.3 ± 6%	0.0040 ± 10%									79.3
Hydrocarbons (as CH_4)[a]	57.1 ± 7%	0.0203 ± 47%	0.268	13 ± 61%	0.00038 ± 20%	0.0055 ± 20%	0.039 ± 20%	0.17 ± 20%	0.025 ± 20%	0.024 ± 20%	71.06
Nitrogen oxides		0.542 ± 107% - 100%	0.01								0.552
Sulfur oxides		0.0176 ± 59%									0.0176
Particulates											
Chemical substances											
Methane	0.67 ± 6%	0.0023 ± 10%									0.6723
Ethane	1.93 ± 92%										1.93
Ethylene	2.57 ± 81%										2.57
Propane and Propylene	55.0 ± 60%		0.022		0.000006 ± 20%						55.0
Butene	0.400 ± 50%										0.400
Benzene	0.146 ± 50%										0.202
Toluene	0.065 ± 50%										0.074
Acrylonitrile	0.039 ± 41%	<0.0015	0.039		0.00042 ± 20%	0.0065 ± 20%	0.046 ± 20%	0.2 ± 20%	0.03 ± 20%		0.807
Acetonitrile	0.625 ± 49%	<0.0015			0.000024 ± 20%						0.687
Hydrogen cyanide	0.275 ± 22%	0.0341 + 428% - 100%	0.35							0.04 ± 20%	0.739
Fumaronitrile				0.036							0.018
Pyridine				5.2 ± 74%							2.58
Propionaldehyde	0.0061 ± 50%										0.0061
Furan	0.467 ± 50%										0.467
Ammonia					0.000006 ± 20%						0.000006
Allyl alcohol	0.024 ± 50%										0.024

[a] Emission factors for total hydrocarbons do not equal the sum of emission factors for all organic materials except methane. To determine the hydrocarbon emission, the methane equivalent emission factors (based on carbon) for each nonmethane organic material are calculated and then summed. (Statement applies to all emission points except deep well pond where 7.8 g/kg of material [two species] were unidentifiable).

[b] Values shown apply to each tank comprising the emission point.

Note: Blanks indicate no emissions present.

TABLE 23. EMISSION FACTORS FOR ACRYLONITRILE MANUFACTURE BY EMISSION POINT (CONTROLLED EMISSIONS)
(g/kg)

Material emitted	Emission point	
	Absorber vent[a]	Deep well pond[b]
Criteria pollutants		
Carbon monoxide	<4.0	
Hydrocarbons	<2.86	1.1 + 117% - 100%
Nitrogen oxides		
Sulfur oxides		
Particulates		
Chemical substances		
Methane	<0.03	
Ethane	<0.1	
Ethylene	<0.1	
Propane and propylene	<3.0	
Butene	<0.02	
Butane		0.06 + 182% - 100%
Methanol		0.16 + 138% - 100%
Pentane		0.04 + 172% - 100%
Acetaldehyde		0.06 + 422% - 100%
Hexane		0.04 + 145% - 100%
Ethanol		0.1 + 315% - 100%
Benzene	<0.07	0.1 + 150% - 100%
Toluene	<0.003	0.02 + 222% - 100%
Acrylonitrile	<0.002	
Acetonitrile	<0.03	
Hydrogen cyanide	<0.01	
Propionaldehyde	<0.0001	
Furan	<0.02	
Allyl alcohol	<0.001	

Note: Blanks indicate no emissions present.

[a] Control efficiency is >95% for thermal oxidizers or catalytic incinerators for the carbon monoxide and hydrocarbon emissions from absorber vent.

[b] Control efficiency is 92% when using a lube oil covering on pond for control of hydrocarbons.

TABLE 24. PLANT PARAMETERS USED IN DETERMINING THE REPRESENTATIVE ACRYLONITRILE SOURCE

Plant parameter	Value	Reference
Technology	SOHIO	3
Catalyst type	41	3
Capacity, metric tons/yr	140,000 ± 50,000	13
Absorber stack height, m	62.8 ± 5.8	3
Incinerator stack height, m	33.5 ± 8.2	3
Flare stack height, m	62.9 ± 25.0	3
Population density, persons/km^2	402	14
Wind speed, m/s	4.5	

The factor 8/24 adjusts the TLV for continuous rather than workday exposure, and the factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers. Thus, the source severity represents the ratio of the maximum mean ground level exposure to the hazard level of exposure for a given pollutant.

The maximum ground level concentration, χ_{max}, is calculated according to Gaussian plume dispersion theory:[21]

$$\chi_{max} = \frac{2\ Q}{\pi H^2 e \bar{u}} \qquad (5)$$

where Q = mass emission rate, g/s
$\bar{u}$ = average wind speed, m/s
H = effective emission height, m
e = 2.72
π = 3.14

Equation 5 yields a value for a short-term averaging time during which the Gaussian plume dispersion equation is valid.

The short-term averaging time was found to be 3 minutes in a study of published data on lateral and vertical diffusion. For a continuously emitting source, the maximum mean ground level concentration for time intervals between 3 minutes and 24 hours can be estimated from the relation:[21]

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_0}{t}\right)^{0.17} \qquad (6)$$

where t_0 = the short-term averaging time or 3 min
t = the averaging time, min

For noncriteria pollutants, the averaging time, t, is 1,440 min (24 hr). For criteria pollutants, the averaging times are those used in the definition of the primary ambient air quality standards. The only exception is NO_x, for which the primary standard averaging time is 1 year. Since Equation 6 is not valid for averaging times of this magnitude, the calculation of $\bar{\chi}_{max}$ for NO_x is based on Equation 5.13 of Reference 21 which estimates the annual average ground level concentration.

Insertion of the average wind speed of 4.5 m/s into the above equations leads to the severity factor equations listed in Table 25 as calculated in Appendix H.

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[21] Turner, D. B. Workbook of Atmospheric Dispersion Estimates. Public Health Service Publication No. 999-AP-26, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1969. 64 pp.

TABLE 25. SOURCE SEVERITY EQUATIONS

Pollutant	Source severity	Equation	Equation in Appendix H
Particulate	$S = 70\ QH^{-2}$	7	H-40
SO_x	$S = 50\ QH^{-2}$	8	H-43
NO_x	$S = 315\ QH^{-2.1}$	9	H-57
Hydrocarbons	$S = 162.5\ QH^{-2}$	10	H-35
CO	$S = 0.78\ QH^{-2}$	11	H-29
All others	$S = 5.5\ QH^{-2}\ (TLV)^{-1}$	12	H-70

Q = emission rate, g/s
H = effective emission height, m
TLV = threshold limit value, g/m^3

The effective emission heights used in the calculations are summarized in Table 26. Stack heights shown for the absorber vent, flare stack, and incinerators were obtained from Reference 3 and mean values are listed in Table 24. Stack heights for the sotrage tanks are listed in Table 11. Emission heights for the product transport loading facility and the fugitive emissions were assumed to be 9.1 m.

TABLE 26. EFFECTIVE EMISSION HEIGHTS USED TO CALCULATE MAXIMUM GROUND LEVEL CONCENTRATIONS

Emission point	Stack height, m[a]
Absorber vent	62.8
Flare stack	62.9
Incinerator	33.5
Product transport loading facility	9.1
Storage tanks	15.2
Fugitive emission	9.1
Deep well pond	9.1

[a] Stack height values represent physical stack heights. Visual observation during sampling showed plume rise to be insignificant.

The emission rates (Q) were obtained from the emission factors in Table 22. The resulting maximum ground level concentrations are tabulated in Table 27. Source severities for uncontrolled and controlled emissions are shown in Tables 28 and 29. In these calculations, intermittent sources, such as fugitive emissions and storage tank vents, were treated as continuous sources with their respective annual emission rates. In addition, it was assumed that Gaussian plume dispersion theory is equally valid

TABLE 27. MAXIMUM GROUND LEVEL CONCENTRATIONS OF ATMOSPHERIC EMISSIONS FROM ACRYLONITRILE MANUFACTURE (UNCONTROLLED EMISSIONS) (mg/m^3)

	Emission point						Storage tank emission point			
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Two product acrylonitrile run-down tanks[a]	Three product acrylonitrile field storage tanks[a]	Off-specification acrylonitrile	Two crude acrylonitrile storage tanks[a]
Criteria pollutants										
Carbon monoxide	4.6	0.00083								
Hydrocarbons	3.3	0.00225	0.024	36	0.0013	0.018	0.046	0.2	0.03	0.04
Nitrogen oxides		0.41	0.0006							
Sulfur oxides		0.0037								
Particulates										
Chemical substances										
Methane	0.039	0.00047								
Ethane	0.11									
Ethylene	0.15									
Propane and propylene	3.2		0.0013		0.00001					
Butene	0.023									
Benzene	0.0085									
Toluene	0.0038									
Acrylonitrile	0.0023	0.00031	0.0020		0.0010	0.018	0.046	0.2	0.03	
Acetonitrile	0.037	0.00031			0.00007					
Hydrogen cyanide	0.016	0.0071	0.02[illegible]							0.04
Fumaronitrile				0.015						
Pyridine				1.3						
Propionaldehyde	0.0003									
Furan	0.027									
Ammonia					0.00001					
Allyl alcohol	0.0014									

Note: Blanks indicate no emissions present.

[a] Values shown apply to each tank comprising the emission point.

TABLE 28. SOURCE SEVERITIES FOR UNCONTROLLED EMISSIONS

	Emission point						Storage tank emission point			
Material emitted	Absorber vent	Incinerator stack	Flare stack	Deep well pond[a]	Fugitive emissions	Product transport loading facility	Product acrylonitrile run-down tanks[b]	acrylonitrile field storage	Off-specification acrylonitrile	Crude acrylonitrile
Criteria pollutants										
Carbon monoxide	0.07	0.000013								
Hydrocarbons[c,d]	10.4	0.002	0.075	98	0.0039	0.0040	0.14	0.63	0.051	0.13
Nitrogen oxides		0.48	0.0023							
Sulfur oxides		0.0035								
Particulates										
Chemical substances										
Methane	0.0058	0.000051								
Ethane	0.0088									
Ethylene	0.013									
Propane and propylene	0.18		0.0001		0.000001					
Butene	0.0010									
Benzene	0.03[e]									
Toluene	0.001									
Acrylonitrile	0.0054	0.00073	0.0054		0.0028	0.043	0.108	0.47	0.071	
Acetonitrile	0.055	0.00047			0.000048					
Hydrogen cyanide	0.15	0.068	0.200							0.94
Fumaronitrile				–[f]						
Pyridine				202						
Propionaldehyde	0.013									
Furan	0.145									
Ammonia					0.000085					
Allyl alcohol	0.030									

[a] Occurs on plant property.

[b] Values shown apply to each tank comprising the emission point.

[c] Hydrocarbons include all organic materials except methane.

[d] Total source severity for nonmethane organic materials will not equal the source severity for hydrocarbons. Source severities for the organic chemicals are based on the toxicity of the chemicals. The hydrocarbon source severity is based on the toxicity of oxidants, which are the products of the photochemical degradation of the organic chemicals.

[e] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene becomes 900.

[f] Indeterminate since a TLV does not exist for this material.

Note: Blanks indicate no emissions present.

TABLE 29. SOURCE SEVERITIES FOR CONTROLLED EMISSIONS

Material emitted	Emission point Absorber vent[a]	 Deep well pond[b,c]
Criteria pollutants		
Carbon monoxide	<0.0035	
Hydrocarbons	<0.52	7.8
Nitrogen oxides		
Sulfur oxides		
Particulates		
Chemical substances		
Methane	<0.005	
Ethane	<0.00044	
Ethylene	<0.00065	
Propane and propylene	<0.009	
Butene	<0.00005	
Butane		0.0068
Methanol		0.18
Pentane		0.0065
Acetaldehyde		0.097
Hexane		0.032
Ethanol		0.015
Benzene	<0.015[d]	0.015[e]
Toluene	<0.00005	0.016
Acrylonitrile	<0.00027	
Acetonitrile	<0.048	
Hydrogen cyanide	<0.0075	
Propionaldehyde	<0.00065	
Furan	<0.0073	
Allyl alcohol	<0.0015	

Note: Blanks indicate no emissions present.

[a] Control efficiency >95% for thermal oxidizers or catalytic incinerators for the carbon monoxide and hydrocarbon emissions from absorber vent.

[b] Control efficiency >92% when using a lube oil covering on pond for control of hydrocarbons.

[c] Occurs on plant property.

[d] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene is <4.5.

[e] Using a TLV of 10^{-6} g/m^3 for suspected carcinogens, as defined by EPA, the source severity for benzene becomes 300.

for all emissions, irrespective of their chemical, physical or topological characteristics. Source severity distributions for the absorber vent are shown in Figure 5, as is the frequency at which a source severity is less than the indicated values.

D. INDUSTRY CONTRIBUTION TO TOTAL ATMOSPHERIC EMISSIONS

The mass emissions of criteria pollutants (particulate, SO_x, NO_x, CO, and hydrocarbons) resulting from acrylonitrile production were calculated using the emission factors from Tables 22 and 23 together with the production capacity data from Table 13. The appropriate emission factor was multiplied by the production capacity nationwide and for each state in which acrylonitrile plants are located. The total mass emissions from all sources nationwide and for each state have been reported.[22] The percent contributions to the total emissions resulting from acrylonitrile production were computed using these values. The results are presented in Table 30 for nationwide emissions, and in Table 31 for individual state emissions.

TABLE 30. NATIONWIDE EMISSIONS OF CRITERIA POLLUTANTS FROM ACRYLONITRILE MANUFACTURE

Criteria pollutant	1976 Nationwide emissions,[a,22] 10^6 metric tons/yr	1976 Emissions from acrylonitrile manufacture, 10^6 metric tons/yr	Acrylonitrile contribution to national total, %
Carbon monoxide	88.130	0.0269	0.030
Hydrocarbons	16.580	0.0249	0.150
Nitrogen oxides	9.269	0.00047	0.005
Sulfur oxides	24.350	0.000015	0.000062
Particulates	129.500	0	0

[a] From all stationary sources.

E. AFFECTED POPULATION

A measure of the population which is exposed to a contaminant concentration exceeding an acceptable level (as defined) near a representative acrylonitrile plant can be obtained by determining (by iteration) the values of x, the distance from the source, for which

$$\frac{\chi(x)}{F} = 1.0 \qquad (13)$$

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[22] Eimutis, E. C., and R. P. Quill. Source Assessment: State-by-State Listing of Criteria Pollutant Emissions. Contract 68-02-1874, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. (Final document submitted to the EPA by Monsanto Research Corporation, June 1977.) 136 pp.

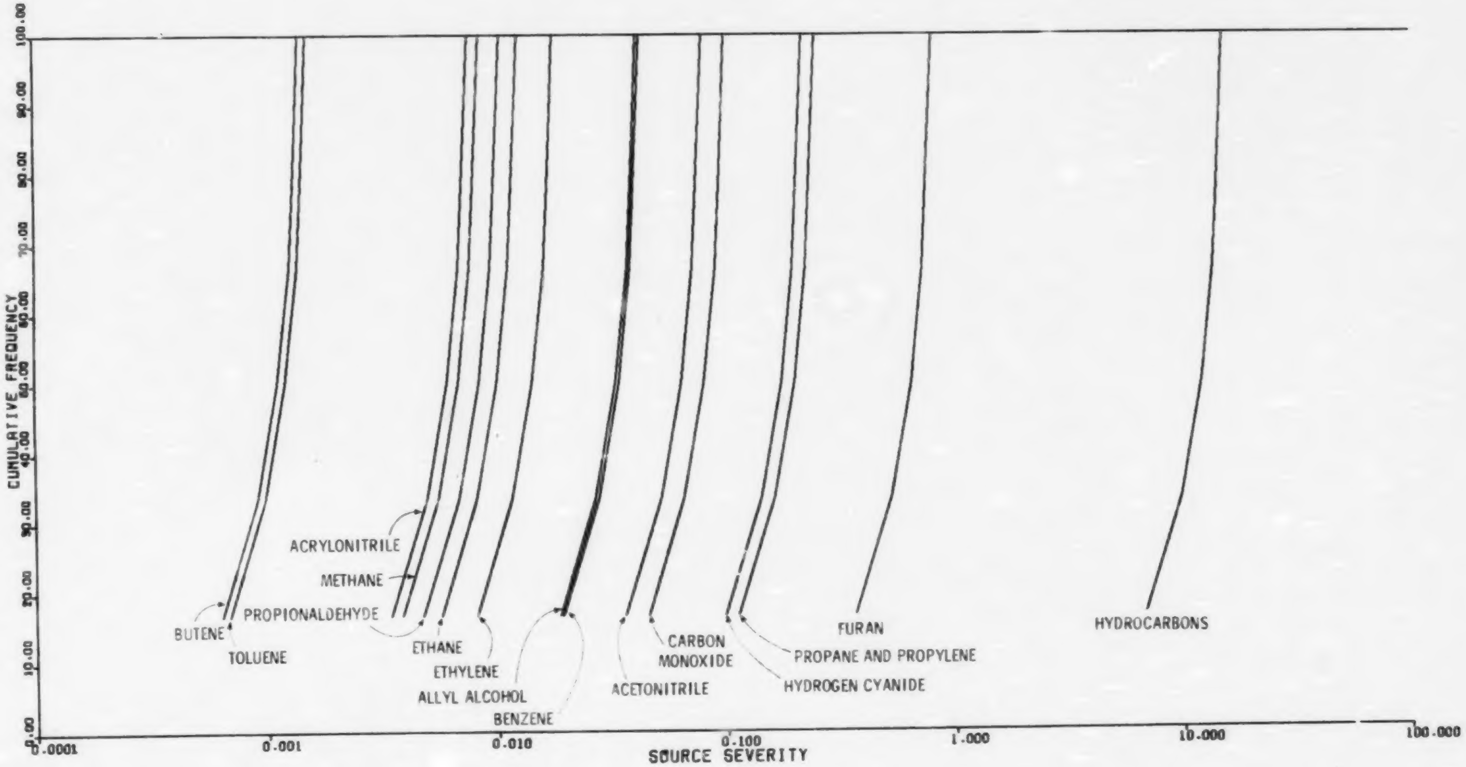

Figure 5. Source severity distributions for uncontrolled emissions in absorber vent gas.

TABLE 31. EMISSIONS OF CRITERIA POLLUTANTS FROM ACRYLONITRILE MANUFACTURE BY STATE

Criteria pollutant	State	Total state emissions,[a,22] 10^6 metric tons/yr	Emissions from acrylonitrile manufacture, 10^6 metric tons/yr	Acrylonitrile contribution to state total, %
Carbon monoxide	Louisiana[b]	0.746	0.0072	0.965
	Ohio[b]	14.370	0.0072	0.050
	Tennessee[b]	0.223	0.0103	4.62
	Texas[c]	1.913	0.0022	0.115
Hydrocarbons	Louisiana[b]	1.009	0.0065	0.644
	Ohio[b]	0.839	0.0065	0.775
	Tennessee[b]	0.258	0.0092	3.57
	Texas[c]	2.158	0.0027	0.124
Nitrogen oxides	Louisiana[b]	0.272	0.00005	0.018
	Ohio[b]	0.684	0.00005	0.0073
	Tennessee[b]	0.290	0.00007	0.0241
	Texas[b]	0.786	0.00030	0.0382
Sulfur oxides	Louisiana[b]	0.323	0.000002	0.0006
	Ohio[b]	2.081	0.000002	0.00009
	Tennessee[b]	0.882	0.000002	0.00023
	Texas[b]	0.938	0.000009	0.0096
Particulates	Louisiana[b]	1.698	0	0
	Ohio[b]	3.157	0	0
	Tennessee[b]	1.763	0	0
	Texas[c]	9.279	0	0

[a] For all stationary sources.

[b] Uncontrolled emissions.

[c] Absorber vent emissions controlled by 95% and deep well emissions controlled by 92%; other emissions uncontrolled.

The value of $\chi(x)$, the ground level concentration, is computed from the equation:[21]

$$\chi(x) = \frac{2.03\ Q}{\sigma_z \bar{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (14)$$

where Q = emission rate, g/s
H = effective emission height, m
x = downwind distance from source, m
$\bar{u}$ = average wind speed (= 4.5 m/s)
σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by:[23]

$$\sigma_z = 0.113\ x^{0.911} \qquad (15)$$

The affected area is then computed as

$$A = \pi(x_2{}^2 - x_1{}^2),\ \text{km}^2 \qquad (16)$$

where x_1 and x_2 are the two roots of Equation 13.

The mean population density, $\bar{D}_P$, is calculated as follows:

$$\bar{D}_P = \frac{\sum_i^n D_{P_i}}{n},\ \text{persons/km}^2 \qquad (17)$$

where D_{P_i} = county population density for plant i
n = number of plants

The product $A \cdot \bar{D}_P$ is designated the "affected population," which was computed for each compound and each source for which the source severity, S, exceeds 1.0. The results are presented in Table 32. In Table 32, dashes indicate that the material shown is not discharged from the emission point listed; hence, there is no possibility for an affected population. Zeros indicate that material is discharged from the emission point but that the resulting ambient levels have source severities ≤ 1.0. The equivalent plant population for the representative plant is 1,600 persons when applying the average county population density (402 persons/km^2) to the plant area (4 km^2). Any affected population $\leq 1,600$

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[23] Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmospheric Dispersion Coefficients. Atmospheric Environment, 6:859-863, November 1972.

TABLE 32. AFFECTED POPULATION[a]

Component	Absorber	Incinerator	Flare stack	Deep well pond	Fugitive emissions	Product transport loading facility	Storage tanks[b]
Carbon monoxide	0	0	-	-	-	-	-
Hydrocarbons	13,300	0	0	1,590	0	-	-
Nitrogen oxides	-	0	0	-	-	-	-
Sulfur oxides	-	0	-	-	-	-	-
Methane	0	0	-	-	-	-	-
Ethane	0	-	-	-	-	-	-
Ethylene	0	-	-	-	-	-	-
Propane and propylene	0	-	0	-	0	-	-
Butene	0	-	-	-	-	-	-
Butanes	-	-	-	0	-	-	-
Pentanes	-	-	-	0	-	-	-
Hexanes	-	-	-	0	-	-	-
Benzene	0	-	-	0	-	-	-
Toluene	0	-	-	0	-	-	-
Acrylonitrile	0	-	0	-	0	0	0
Acetonitrile	0	-	-	-	0	-	0
Hydrogen cyanide	0	0	0	-	-	-	-
Fumaronitrile	-	-	-	0	-	-	-
Pyridine	-	-	-	156	-	-	-
Propionaldehyde	0	-	-	-	-	-	-
Furan	0	-	-	-	-	-	-
Ammonia	-	-	-	-	0	-	-
Allyl alcohol	0	-	-	-	-	-	-
Acetaldehyde	0	-	-	-	-	-	-
Methanol	0	-	-	-	-	-	-
Ethanol	0	-	-	-	-	-	-

[a] Dashes indicate that material shown is not discharged from emission point listed; zeros indicate that ambient levels resulting from discharged material produce source severities ≤ 1.0.

[b] Value shown is largest value for all storage tanks.

indicates that the exposure occurs on the plant site and not on the surrounding community. The total number of persons affected by a representative plant is 13,300. This affected population represents the number of persons exposed to nonmethane hydrocarbon emissions which exceed the primary ambient air quality standard (guideline) for hydrocarbons (160×10^{-6} g/m^3); 96% of the total hydrocarbons emission is due to propane and propylene emissions. No nonplant persons are exposed to source severities >1.0 nitrile emissions.

F. TRENDS IN ACRYLONITRILE PLANT EMISSIONS

In 1973, 613,700 metric tons of acrylonitrile were produced. As discussed in Section VI, a total of 1.3×10^6 metric tons of acrylonitrile is expected to be produced in 1978.[2] This corresponds to an overall increase in acrylonitrile manufacture of 112% for the 5-year period 1973 to 1978. Atmospheric emissions from the acrylonitrile absorber vent will follow the trends presented in Table 33 and Figure 6 based on anticipated production and emission factors.

TABLE 33. ANNUAL EMISSIONS OF CRITERIA POLLUTANTS FROM ACRYLONITRILE PLANTS

Year	Carbon monoxide, 10^3 metric tons	Total hydrocarbons, 10^3 metric tons
1967	54[a]	47[a]
1968	82[a]	72[a]
1969	93[a]	81[a]
1970	84[a]	73[a]
1971	79[a]	69[a]
1972	80[b]	69[b]
1973	84[c]	73[c]
1974	87[c]	76[d]
1975	97[d]	85[d]
1976	26.9[d,e]	24.9[d,e]
1977	30.8[d,e]	28.6[d,e]
1978	35.0[d,e]	32.3[d,e]
1979	40.4[d,e]	37.5[d,e]
1980	48.5[d,e]	44.9[d,e]

[a] All capacity based on use of Catalyst 21.

[b] 33% Capacity based on Catalyst 41, balance on Catalyst 21.

[c] 66% Capacity based on Catalyst 41, balance on Catalyst 21.

[d] All capacity based on Catalyst 41.

[e] 95% Control of carbon monoxide and hydrocarbon emissions from absorber vent for plants in Texas.

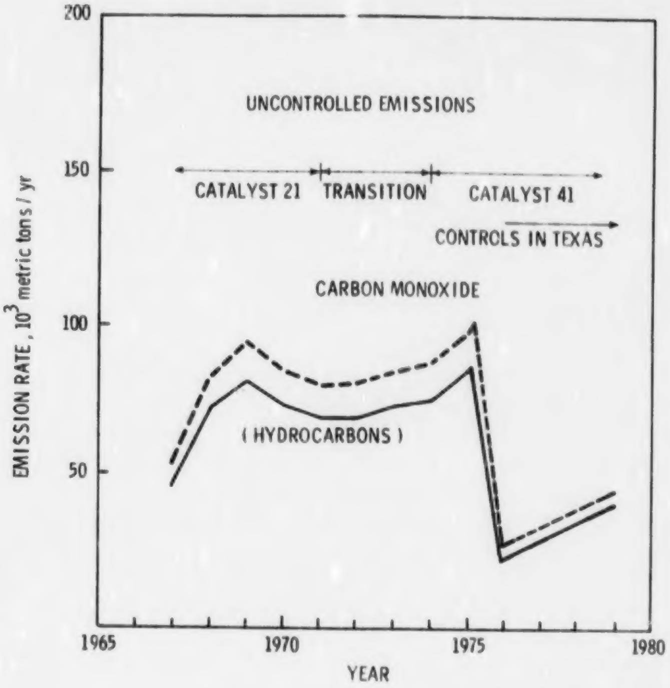


Figure 6. Annual yearly mass of emission of criteria pollutants from acrylonitrile manufacture.

The emission rate trends are not shown for sulfur oxides and nitrogen oxides since these emissions each represent less than 1,000 metric tons per year as shown in Table 30. However, during this period, all plants operating in Texas will be required to install emissions control equipment which will result in reductions in carbon monoxide and hydrocarbon emissions. Control efficiencies for both carbon monoxide and hydrocarbons have been demonstrated to be greater than 95% through field sampling. Therefore, the mass of emissions from acrylonitrile plants will decrease 58% for carbon monoxide and 56% for hydrocarbons over the period 1973 to 1978. This is due to the implementation of air pollution control equipment on these plants as required by state regulatory agencies.

SECTION V

CONTROL TECHNOLOGY

A. STATE OF THE ART

As of January 1, 1976, only Monsanto Company's plant in Alvin, Texas was using any form of air pollution control for absorber vent emissions. Du Pont's plant located in Beaumont, Texas will be bringing absorber vent emissions control equipment on stream in 1976. Both of these plants are using combustion devices to reduce emissions of carbon monoxide and hydrocarbons to levels permitted by the Texas Air Control Board. Monsanto's control device is a thermal oxidizer while Du Pont's device will be a catalytic oxidizer.

Monsanto uses a thermal oxidizer for by-product hydrogen cyanide and acetonitrile disposal as well as the air pollution control device for absorber vent gas. The unit is a thermal oxidizer used solely for the incineration of combustibles without waste heat recovery or steam generation. Figure 7 is a schematic flow diagram for the unit.

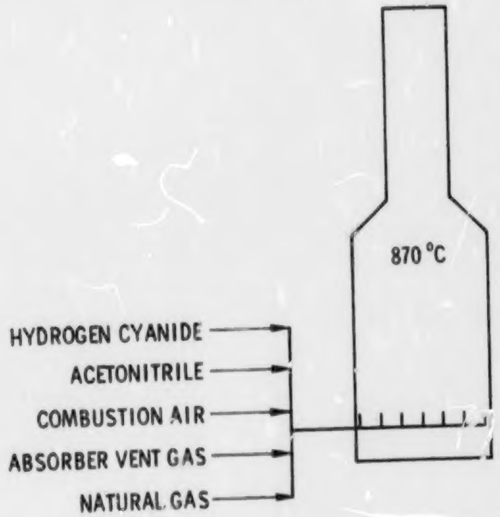


Figure 7. Schematic diagram for a combination byproduct incinerator/absorber vent gas thermal oxidizer system.

The thermal oxidizer operates at 870°C and obtains >95% removal of carbon monoxide and >95% combustion of total hydrocarbons. Based on hydrocarbon content of absorber vent gas and assuming 100% combustion of liquid organics and natural gas fuel, a reduction in absorber vent hydrocarbons of >95% is obtained.

B. FUTURE CONSIDERATIONS

Since hydrocarbon emissions result from incomplete conversion in the reactor, the acrylonitrile industry has thus far concentrated its efforts for reducing emissions on the development of more selective catalysts. Such catalysts would increase acrylonitrile production while lowering the amount of by-products which are vented. These efforts have been initiated because of escalating propylene costs and tighter propylene supplies.[3]

As a result of the current concern for environmental quality, various other methods of emission control have been suggested. The devices recommended by Schwartz, et al,[3] fall into the category of combustion devices. These include CO-boilers, thermal incinerators, catalytic incineration, and plume burners.[3]

1. Waste-Heat Recovery Boilers

Waste-heat recovery boilers are among the more efficient methods of reducing hydrocarbons and carbon monoxide emissions, as evidenced by their extensive use in petroleum refineries. However, by-product steam credit may not offset their operating cost for use in acrylonitrile plants. Currently, sufficient quantities of steam are provided by reactor cooling coils and waste heat recovery from the reactor effluent. This steam is used to drive the air blower and provide process steam requirements. Therefore, most, if not all, of the steam produced would have to be exported. Considering the current trend toward ever higher fuel prices, exporting steam from emission control devices may be feasible in the future. However, it may not be economical to export steam at today's fuel prices. Transportation costs for generated steam export may not be a limiting factor since all acrylonitrile plants are located near either petroleum refineries or large petrochemical complexes, both of which are large consumers of steam.[3]

Table 34 presents a typical material balance for a CO-boiler designed to process the absorber vent gas. Figure 8 is a schematic flow diagram for a waste-heat recovery boiler. The data in the table are based on a 980°C combustion zone temperature and 4 mole percent oxygen (dry bases) in the stack gas.[3]

No existing acrylonitrile plant in the U.S. employs waste-heat recovery boilers on this vent stream (January 1, 1976). Therefore, it is difficult to accurately predict equipment performance in this application. Based upon applications in other areas, the following potential problems exist with off-gas burning in waste-heat recovery boilers.[3]

TABLE 34. TYPICAL MATERIAL BALANCE FOR A CO-BOILER EMISSION CONTROL SYSTEM[3] (kg/hr)

Component	Process vent gas	Combustion air	Natural gas	Flue gas
Carbon dioxide	5,067			20,006
Carbon monoxide	2,026			
Methane			1,130	
Ethane			249	
Propylene	887			
Propane	1,585			
Hydrogen cyanide	14			
Acrylonitrile	112			
Acetonitrile	43			
Nitrogen	93,919	53,939	117	147,973
Oxygen	7,105	16,379		7,639
Water	6,437	932		14,199
Nitrogen oxides				124
Total kg/hr	117,195	71,250	1,496	189,941
Total standard m^3/s	27.5			44.5

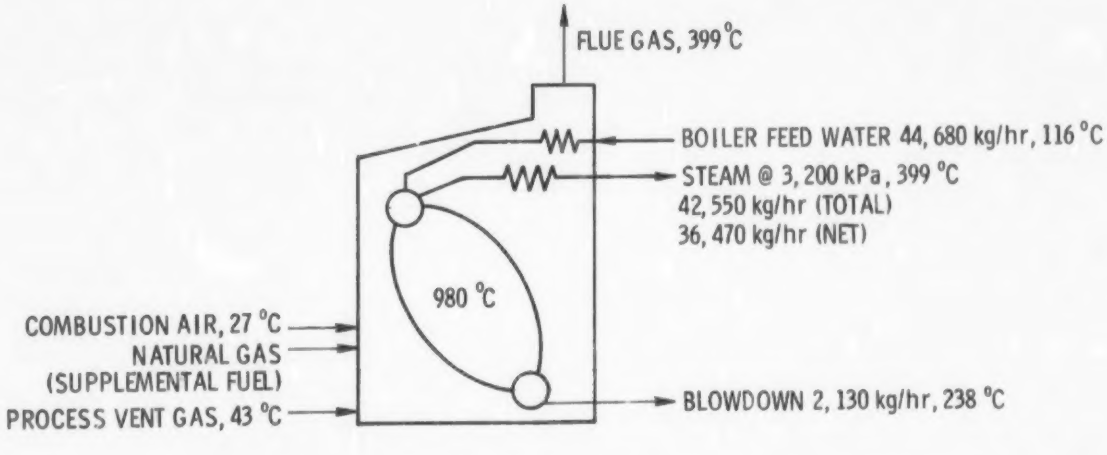

FLUE GAS, 399 °C
BOILER FEED WATER 44,680 kg/hr, 116 °C
STEAM @ 3,200 kPa, 399 °C
42,550 kg/hr (TOTAL)
36,470 kg/hr (NET)
980 °C
COMBUSTION AIR, 27 °C
NATURAL GAS
(SUPPLEMENTAL FUEL)
PROCESS VENT GAS, 43 °C
BLOWDOWN 2,130 kg/hr, 238 °C

Figure 8. Typical flow diagram for a CO-boiler emission control system.[3]

- Vent gas is available only at low pressure.
- Investment for required blowers, large diameter pipes and valves, burning equipment, control systems, and steam utilization systems is high.
- Because the gas has a low heating value (1.3 to 1.9 MJ/m^3) due to a high (95%) noncombustibles content, 30% to 35% of the total heat requirement must be added as supplemental fuel to achieve complete combustion.

2. Thermal Incinerators

Figure 9 presents a schematic flow diagram for a thermal incinerator. Table 35 presents a material balance for this type of control device. Data in this table are based on the same combustion zone operating conditions used for the CO-boiler. Heat generated from burning the process vent gas plus feed effluent heat exchange is sufficient to obtain the desired operating temperature. Burning of off-gas in a conventional thermal incinerator results in burning and combustion efficiency problems similar to those anticipated for a CO-boiler.[3]

3. Catalytic Incineration

A conventional catalytic incinerator could reduce pollutants to levels similar to those obtained with a thermal unit. The catalytic incinerator would operate at lower temperature (480°C to 650°C) and therefore would produce less NO_x.[3]

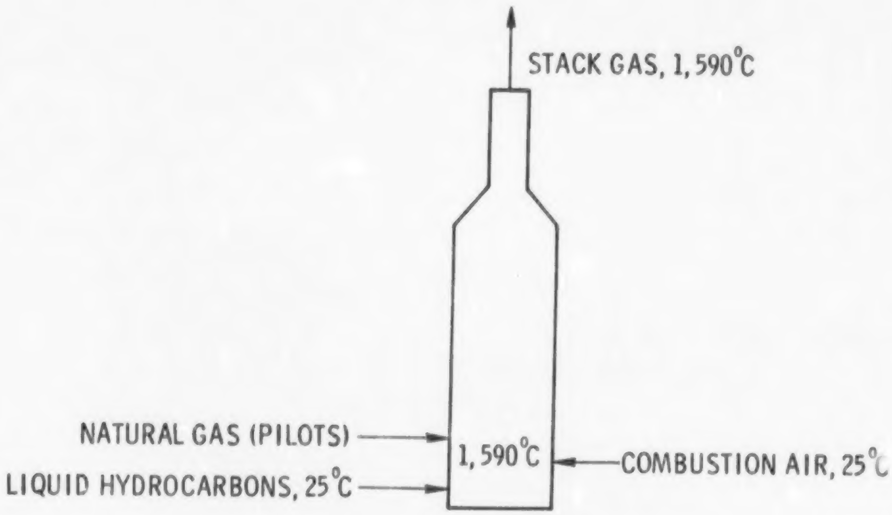


Figure 9. Thermal incinerator for an acrylonitrile plant.[3]

TABLE 35. TYPICAL MATERIAL BALANCE FOR A THERMAL INCINERATOR FOR BY-PRODUCT STREAMS[3] (kg/hr)

Component	Liquid hydrocarbons			Combustion air	Stack gas
	Hydro-cyanic acid	Aceto-nitrile	Heavy ends		
Hydrogen cyanide	953	0	0	0	0
Acrylonitrile	5	0	0	0	0
Acetonitrile	0	1,090	23	0	0
Sulfuric acid	1	0	0	0	1
Organic polymers	0	0	68	0	0
Carbon dioxide	0	0	0	0	4,152
Nitrogen	0	0	0	16,564	17,420
Oxygen	0	0	0	5,029	958
Water	3	0	0	285	1,433
Nitrogen oxides	0	0	0	0	57
Total kg/hr	962	1,090	91	21,878	24,021
Total m^3/min	1.4	1.42	0.09	0	0
Total standard m^3/s	0	0	0	1,129	1,225

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PROCESS TECHNOLOGY

Acrylonitrile can be produced on a commercial scale using any of the following feedstocks: ethylene oxide, acetylene and propylene (using either nitric oxide or ammonia). Figure 10 shows the extent of use of the various feedstock types. As shown, the ammoxidation of propylene was the only process in use in 1975. The use of various feedstocks has been the result of process improvements and economics. A brief description of each technology type is given below.[2]

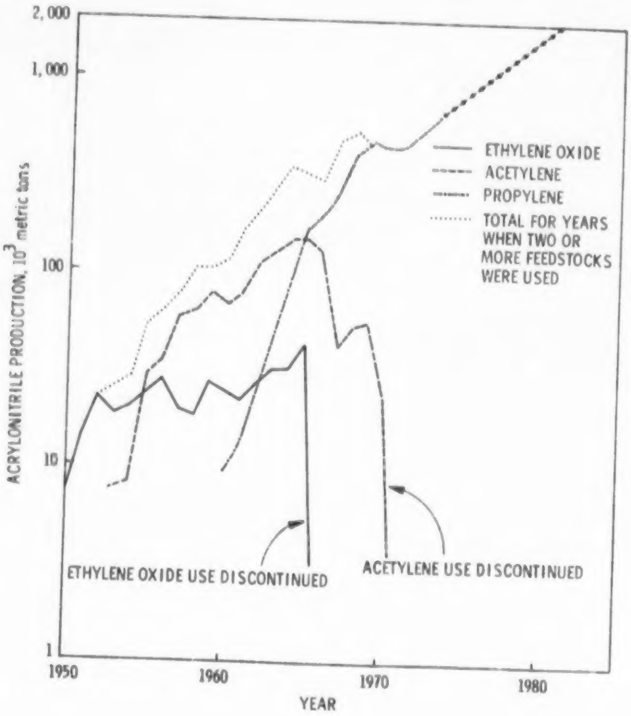
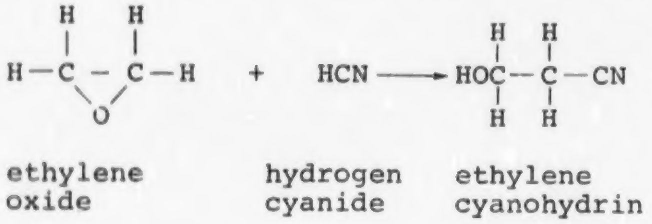


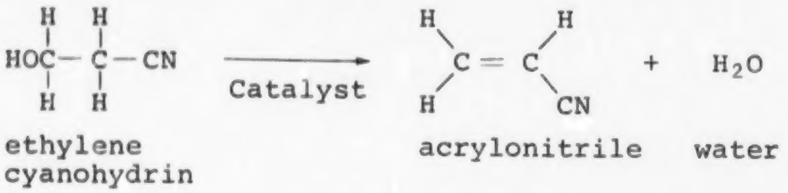
Figure 10. Acrylonitrile industry growth.[2]

1. Ethylene Oxide Process

Acrylonitrile was first produced by the catalytic dehydration of ethylene cyanohydrin derived from ethylene oxide and hydrogen cyanide. The chemical reactions used for this process are:[2]


ethylene oxide
hydrogen cyanide
ethylene cyanohydrin

(18)

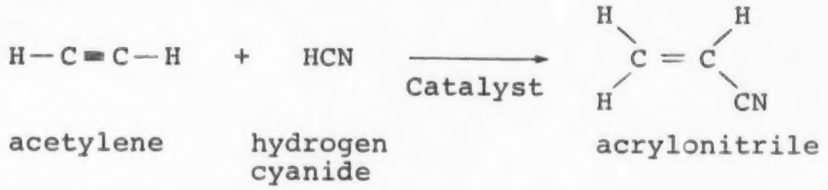

Catalyst
ethylene cyanohydrin
acrylonitrile
water

(19)

American Cyanamid Company (Warners, New Jersey) and Union Carbide Corporation (Institute, West Virginia) have produced acrylonitrile using this technology. However, the ethylene oxide process is no longer used; American Cyanamid and Union Carbide shut down operations in 1956 and 1966, respectively.[2]

2. Acetylene Process

The following catalytic reaction of acetylene and hydrogen cyanide over a cuprous chloride catalyst has been used to produce acrylonitrile:[1,2]

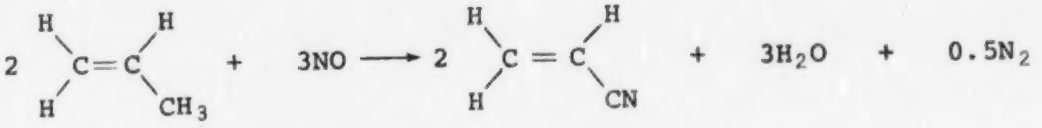

Catalyst
acetylene
hydrogen cyanide
acrylonitrile

(20)

Three companies that have utilized the above technology (from 1953 to 1970) are Du Pont, American Cyanamid and Monsanto.[2]

3. Propylene and Nitric Oxide Process

The Explosives Department of Du Pont has produced acrylonitrile by the catalytic reaction of propylene with nitric oxide:



(21)

propylene nitric oxide acrylonitrile

This process was used through mid-1966 at Du Pont's Beaumont, Texas plant.

4. Ammoxidation of Propylene

Ammoxidation of propylene via the SOHIO process has been used for all acrylonitrile production since 1971. The process mechanisms accounting for all acrylonitrile production through 1975 have been discussed in Section III. Improvements made in the ammoxidation process are discussed here. (From References 2 and 3, and a personal communication, T. W. Hughes of Monsanto Research Corporation and J. Killen of Vistron Corporation, October 3, 1974.)

Process refinement has resulted from catalyst improvements. Overall, the SOHIO process has used three types of catalyst, designated Catalyst A, Catalyst 21, and Catalyst 41. From 1960 to 1967, a bismuth/molybdenum catalyst (Catalyst A) was used. Yields from this catalyst are reported to have been 0.73 kg of acrylonitrile, 0.11 kg of acetonitrile and 0.13 kg of hydrogen cyanide per kg of propylene feed.[2]

From 1967 through 1973, a catalyst based on depleted uranium (Catalyst 21) was used. Reported yields for this catalyst are 0.85 kg of acrylonitrile, 0.10 kg of acetonitrile and 0.10 kg of hydrogen cyanide per kg of propylene.[2,3]

A uranium-free catalyst based on bismuth phosphomolybdate (Catalyst 41) has been used since 1972. Yields for this catalyst are essentially the same as those for Catalyst 21. However, Catalyst 41 utilizes ammonia more effectively so that less excess ammonia is required. Air requirements are also lower for Catalyst 41 than for Catalyst 21, and this increases the capacity of existing plants by 10% to 35% at the same reactor space velocities. Table 36 shows the yields of products formed using the various catalyst types.[2,3]

5. Propane Ammoxidation

Production of acrylonitrile via the ammoxidation of propane has been developed on a pilot scale by Davy Powergas Ltd. and by Imperial Chemical Industries Ltd. The process catalytically reacts propane and ammonia. Catalyst reaction conditions and yields in this process are similar to those in propylene

TABLE 36. EFFECT OF CATALYST IMPROVEMENTS ON ACRYLONITRILE MANUFACTURE VIA AMMOXIDATION OF PROPYLENE[3]

Catalyst type	First year of use	Reactor yields, kg/kg propylene			
		Acrylonitrile	Acetonitrile	Hydrogen cyanide	Ammonium sulfate
A	1960	0.73	0.11	0.13	0.2
21	1967	0.85	0.10	0.10	0.20
41	1972	0.85	0.10	0.10	0.11

ammoxidation. Propane ammoxidation differs from propylene ammoxidation in the type of catalysts employed and the use of a propane recovery and recycle system.[2]

The relative cost and availability of propane versus propylene will be the determining factors in deciding on which feedstock to use in the future. Companies producing acrylonitrile believe that the propane-based process is too expensive (due to utility costs for propane recycle) compared to the propylene ammoxidation process to be widely used for acrylonitrile production.[2]

B. MARKETING STRENGTHS AND WEAKNESSES

Chief uses for acrylonitrile are in the production of acrylic fibers and plastics. A flow diagram showing the uses of acrylonitrile is presented in Figure 11. The demand for acrylic fibers and plastics continues to grow with no sign of easing. In 1973, acrylic fiber production was 3.36 x 10^5 metric tons, up 19% from 1972 (indicating a decline in reserves), and thus required 3.7 x 10^5 metric tons of acrylonitrile or about 60% of all acrylonitrile production. Acrylic fibers should continue to grow at about 7%/yr through the next 5 years.[24-26]

Demand for acrylonitrile-based plastics [notably acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins] is growing faster than production capacity. The 1973 production of ABS and SAN resins was approximately 4.53 x 10^5 metric tons, requiring about 1.36 x 10^5 metric tons of acrylonitrile. The 4-year (ending in 1973) growth rate has been about 15%/yr.

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[24] Stobaugh, R. B., et al. Acrylonitrile - How, Where, Who, Future. Hydrocarbon Processing, 50:109-120, January 1971.

[25] Acrylonitrile (SOHIO Process). Hydrocarbon Processing, 52:99, November 1973.

[26] Chemical Profile: Acrylonitrile. Chemical Marketing Reporter, 205(50):9, May 1974.

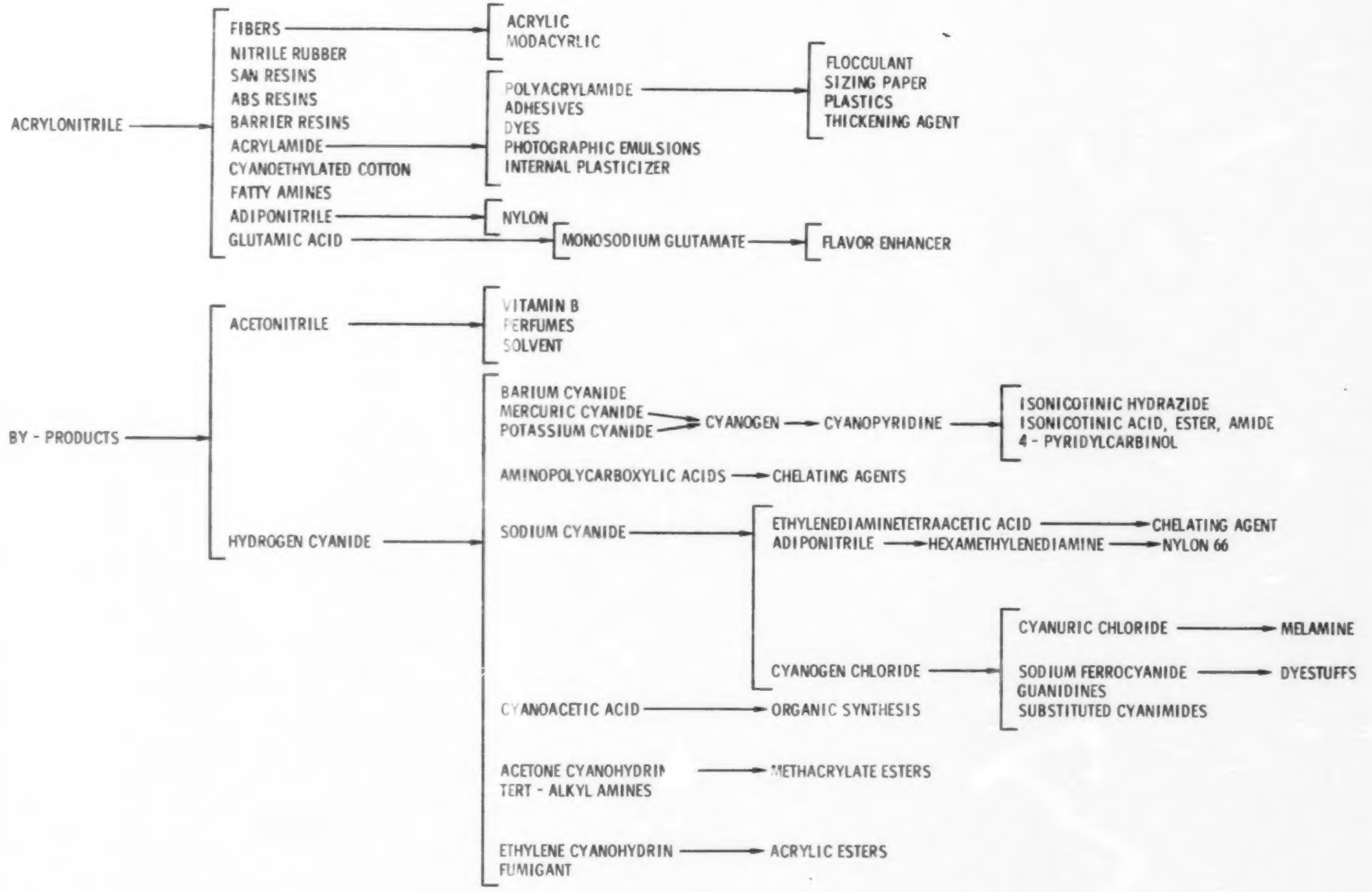
ACRYLONITRILE
FIBERS
NITRILE RUBBER
SAN RESINS
ABS RESINS
BARRIER RESINS
ACRYLAMIDE
CYANOETHYLATED COTTON
FATTY AMINES
ADIPONITRILE
GLUTAMIC ACID
ACRYLIC
MODACYRLIC
POLYACRYLAMIDE
ADHESIVES
DYES
PHOTOGRAPHIC EMULSIONS
INTERNAL PLASTICIZER
FLOCCULANT
SIZING PAPER
PLASTICS
THICKENING AGENT
NYLON
MONOSODIUM GLUTAMATE
FLAVOR ENHANCER
BY - PRODUCTS
ACETONITRILE
VITAMIN B
PERFUMES
SOLVENT
HYDROGEN CYANIDE
BARIUM CYANIDE
MERCURIC CYANIDE
POTASSIUM CYANIDE
CYANOGEN
CYANOPYRIDINE
ISONICOTINIC HYDRAZIDE
ISONICOTINIC ACID, ESTER, AMIDE
4 - PYRIDYLCARBINOL
AMINOPOLYCARBOXYLIC ACIDS
CHELATING AGENTS
SODIUM CYANIDE
ETHYLENEDIAMINETETRAACETIC ACID
CHELATING AGENT
ADIPONITRILE
HEXAMETHYLENEDIAMINE
NYLON 66
CYANOGEN CHLORIDE
CYANURIC CHLORIDE
MELAMINE
SODIUM FERROCYANIDE
DYESTUFFS
GUANIDINES
SUBSTITUTED CYANIMIDES
CYANOACETIC ACID
ORGANIC SYNTHESIS
ACETONE CYANOHYDRIN
TERT - ALKYL AMINES
METHACRYLATE ESTERS
ETHYLENE CYANOHYDRIN
FUMIGANT
ACRYLIC ESTERS

Figure 11. Acrylonitrile markets.[2]

Combined consumption of ABS and SAN in 1973 was 4.77 x 10^5 metric tons, indicating a drop in inventories. Shortage of both styrene and butadiene may limit the growth in this area for the next few years.

Development of barrier resins by Monsanto, Du Pont, and Vistron for plastic soft drink bottles should also increase the demand for acrylonitrile in the plastics industry.[24-26] Demand in this new marketing outlet for acrylonitrile is so great that new plant expansions and construction have been completed. Monsanto Company is expanding its new Cycle-Safe® polymer unit at Springfield, Massachusetts and a new bottle fabrication plant at South Windsor, Connecticut. In addition, Monsanto has begun production at three new bottle plants.[27] Vistron has built a $9 million plant to produce its barrier resin, Barex 210.[26]

Other end-uses for acrylonitrile are seen to grow more slowly than acrylic fibers and plastics. Nitrile rubber, used in hoses, seals, and gaskets, should show a more limited growth (5%/yr), and will decline from its present 5% of total acrylonitrile consumption.

Use of acrylonitrile in nylon production (from acrylonitrile via adiponitrile) remains fairly limited in acceptance. Export of acrylonitrile should remain constant at less than 4.5 x 10^4 metric ton/yr. Export could decline, however, if foreign propylene prices drop below domestic prices.[24-26]

With the increasing demand for acrylonitrile products, the demand for acrylonitrile itself should increase through 1978. The 1978 demand is predicted to be 9.99 x 10^5 metric tons, compared to the 1974 demand of 6.17 x 10^5 metric tons and 6.81 x 10^5 metric tons in 1975. The historical (1963-1973) growth rate of acrylonitrile has been 11.5%/yr; however, this should decrease slightly to ~10%/yr through 1978.[25] To meet the increasing demand for acrylonitrile, industry had several capacity expansions come on stream in 1976 which increased the total industry production capability to 9.31 x 10^5 metric tons/yr in 1977.[25,26] Production capability will, however, still fall short of demand.

The major weakness of the acrylonitrile market is the total dependence of the SOHIO process on propylene which has recently been in tight supply. Propylene is a by-product of refinery cracking and a co-product in ethylene manufacture. Producers can affect the supply by favoring either gasoline production or ethylene production at the expense of propylene production, or vice versa. The availability of refinery propylene is also decreasing because of the use of hydro-crackers (with lower olefin yields) and zeolite catalysts in petroleum catalytic crackers (with lower propane/propylene yields). Refinery production of propylene will probably not increase with expanded refinery capacities. These effects will increase the price of propylene to the chemical user. Propylene production in ethylene plants is limited because of tight supply of raw materials, primarily naphtha (valuable in gasoline production) and propane. Competing with acrylonitrile for the limited supply of propylene are isopropanol, propylene oxide, polypropylene and cumene - all fast-growing products.[24-26]

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[27] Monsanto is Bullish on Acrylo. Chemical Week, 114(25):33, June 1974.

European conditions, however, are different. The lower demand for gasoline and less catcracking capacity result in a higher supply of naphtha. European ethylene plants operate on naphtha and produce relatively large volumes of propylene. The future of domestic acrylonitrile production is thus closely tied in with the European propylene situation.[24]

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APPENDIX A

FIELD SAMPLING RESULTS FOR ABSORBER VENT GAS

The absorber vent emissions data on the following page can be used to determine the decrease in nitrogen emissions, hence, reactor air feed rate. Air feed rate, ammonia feed rate, and propylene feed rate can be used to determine the increase in acrylonitrile plant capacity of a fixed superficial linear velocity in the reactor.

Increase in capacity due to Catalyst 41 use can be determined by the following equation.

$$\frac{\text{Capacity Catalyst 41}}{\text{Capacity Catalyst 21}} = \frac{\text{total moles reactor feed for Catalyst 21}}{\text{total moles reactor feed for Catalyst 41}}$$

$$= \frac{(\text{moles } C_3H_6)_{21} + (\text{moles } NH_3)_{21} + (\text{moles air})_{21}}{(\text{moles } C_3H_6)_{41} + (\text{moles } NH_3)_{41} + (\text{moles air})_{41}}$$

$$= \frac{1 + 1.15 + 10.5}{1 + 1.06 + 8.40}$$

$$= \frac{12.65}{10.46}$$

$$= 1.21 \text{ or } 21\% \text{ increase in capacity}$$

Reference 3 indicates that the increase in capacity can vary from 10% to 35%.

TABLE A-1. ABSORBER VENT EMISSION FACTORS (UNCONTROLLED EMISSIONS)[a] (g/kg of product acrylonitrile)

Material emitted	Average
Inert gases	
Nitrogen	5,865
Oxygen	206
Carbon dioxide	184.5
Water	921.5
Criteria pollutants	
Carbon monoxide	79.3 ± 6.3%[b]
Hydrocarbons[c]	57.1 ± 6.8%
Chemical substances	
Methane	0.672 ± 28%
Ethane	1.93 ± 93%
Ethylene	2.57 ± 81%
Propane and propylene	55.0 ± 85%
Acrylonitrile	0.039 ± 40%
Acetonitrile	0.625 ± 49%
Hydrogen cyanide	0.275 ± 22%
Propionaldehyde	0.0061 ± 50%
Furan	0.467 ± 71%
Benzene	0.146 ± 71%
Toluene	0.065 ± 50%
Allyl alcohol	0.024 ± 50%
Butene	0.400 ± 50%

[a] The values presented in this table represent a composite of the emissions data obtained by sampling uncontrolled emissions from two acrylonitrile plant absorber vents.

[b] Uncertainty for average of two plants =

$$\sqrt{\text{Uncertainty}_{\text{Plant A}}{}^2 + \text{Uncertainty}_{\text{Plant B}}{}^2}$$

[c] "Hydrocarbons" include all organic materials except methane.

APPENDIX B

FIELD SAMPLING RESULTS FOR INCINERATOR STACK GASES

TABLE B-1. INCINERATOR STACK GAS EMISSION FACTORS (g/kg)

Material emitted	Value
Criteria pollutants	
Carbon monoxide	0.004 ± 10%
Hydrocarbons	0.0203 ± 50%
Nitrogen oxides	0.542 ± 23%
Sulfur oxides	0.0176 ± 49%
Chemical substances	
Methane	0.0023 ± 50%
Acrylonitrile	<0.0015
Acetonitrile	<0.0015
Hydrogen cyanide	0.34 + 428% - 100%

APPENDIX C

FIELD SAMPLING RESULTS FOR DEEP WELL POND EMISSIONS

TABLE C-1. DEEP WELL POND EMISSION FACTORS
(g/kg)

Material emitted	Plant A[a]	Plant B[b]
Criteria pollutants		
Hydrocarbons	13 ± 61%	1.1 ± 117%
Chemical substances		
Fumaronitrile	0.036	–[c]
Pyridine	5.2 ± 74%	–[c]
Butanes	–[c]	0.06 + 182% - 100%
Pentane	–[c]	0.04 + 172% - 100%
Hexanes	–[c]	0.04 + 145% - 100%
Benzene	–[c]	0.1 + 150% - 100%
Toluene	–[c]	0.02 + 222% - 100%
Methanol	–[c]	0.2 + 138% - 100%
Acetaldehyde	–[c]	0.06 + 423% - 100%
Ethanol	–[c]	0.1 + 315% - 100%
Others[d]	7.8 ± 75%	–[c]

[a] Uncontrolled emissions from deep well pond.

[b] Controlled emissions using lube oil cover on pond.

[c] Not detected at 0.5 ppm level.

[d] Unidentified.

APPENDIX D

REFERENCE 3 DATA FOR FLARE STACK EMISSIONS

TABLE D-1. FLARE STACK EMISSION FACTORS[3]
(g/kg)

	Plant							
Component	51-1	51-2	51-3	51-4	Mean	Standard deviation	Relative uncertainty	Percent uncertainty
Total flow	43.0	105	156	90	98.5	46.55	74.06	75
Nitrogen	-[a]	78	-[a]	67	72.5	7.78	69.9	96
Oxygen	-[a]	2	-[a]	-[b]	2	-[c]	-[c]	-[c]
Carbon dioxide	-[a]	14	-[a]	18	16	2.83	25.41	158
Water	-[a]	11	-[a]	5	8	4.24	38.12	476
Nitrogen oxides	-[b]	-[d]	-[b]	0.01	0.01	-[c]	-[c]	-[c]

[a] Identified by plant, but only qualitatively.

[b] Not reported.

[c] Not determined.

[d] Trace.

APPENDIX E

STORAGE TANK EMISSION FACTOR CALCULATIONS

The procedure for calculating the atmospheric emissions from fixed roof storage tanks is outlined in this section. Nonmetric units are utilized because they represent the form of the data used in the actual calculations. The equations discussed below were developed and reported in API Bulletins.[28-32]

Storage tank emissions consist of breathing losses and working losses. Breathing losses are caused by daily changes in ambient temperature while working losses are caused by the filling and emptying of the tanks. The calculations are performed in steps as described below. All losses are calculated as equivalent gasoline losses and then converted to specific petrochemical losses.

Step 1. Calculate the equivalent gasoline breathing loss:

$$L_y = \left(\frac{24}{1,000}\right)\left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} (H')^{0.51} (\Delta T)^{0.50} F_p C \qquad \text{(E-1)}$$

---

[28] Evaporation Loss from Fixed Roof Tanks. Bulletin 2518, American Petroleum Institute, New York, New York, 1962. 38 pp.

[29] Use of Variable Vapor Space Systems to Reduce Evaporation Loss. Bulletin 2520, American Petroleum Institute, New York, New York, 1964. 14 pp.

[30] Petrochemical Evaporation Loss from Storage Tanks. Bulletin 2523, American Petroleum Institute, New York, New York, 1969. 14 pp.

[31] Evaporation Loss from Floating Roof Tanks. Bulletin 2517, American Petroleum Institute, New York, New York, 1962. 13 pp.

[32] Evaporation Loss in the Petroleum Industry - Causes and Control. Bulletin 2513, American Petroleum Institute, New York, New York, 1959. 57 pp.

where L_y = equivalent gasoline breathing loss, bbl/yr

P = vapor pressure of material stored at bulk temperature, psia

D = tank diameter, ft

H' = tank outage, ft

ΔT = average ambient temperature change, °F

F_P = paint factor

C = diameter factor

The bulk temperature of stored material was taken to be 69°F for all storage tanks. This temperature was obtained by adding 5°F to the ambient temperature (64°F), as recommended in References 28-32 for tanks held at ambient temperature. The ambient temperature of 64°F was used because it is the national mean ambient temperature.

Tank diameters were computed by assuming a height of 50 ft for all tanks. The tank outage, i.e., freeboard, was taken as one-half the tank height, or 25 ft.

The average ambient temperature change, ΔT, was taken as 20°F, which is the national average value. The paint factor, F_P, was assumed equal to unity or the value for white paint in good condition. This factor can be as high as 14.6 for gray surfaces. The diameter factor, C, is equal to unity for tanks 30 ft or larger in diameter. For smaller tanks, the value is obtained from a graph given in Reference 29, and is between 0.25 and 1.0.

Step 2. Calculate the equivalent gasoline working loss:

$$F_g = \left(\frac{3}{10,000}\right) PVNK_T \qquad \text{(E-2)}$$

where F_g = equivalent gasoline working loss, bbl/yr

V = tank capacity, bbl

N = number of turnovers per year

K_T = turnover factor = 1.0 for $N \leq 36$

$= \dfrac{180 + N}{6N}$ for $N > 36$

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + F_g \qquad \text{(E-3)}$$

Step 4. Compute petrochemical losses:

$$L = 0.08\left(\frac{M}{W}\right)L_g \qquad \text{(E-4)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of chemical stored
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factor:

$$L_1 = L(42)(W) \qquad \text{(E-5)}$$

$$E' = \frac{L_1}{Cap} \qquad \text{(E-6)}$$

$$E = \frac{E'}{2} \qquad \text{(E-7)}$$

where L_1 = petrochemical loss, lb/yr
Cap = production capacity, ton/yr
E' = emission factor, lb/ton
E = emission factor, g/kg

Using the above procedure and the storage tank input data shown in Table E-1, the emissions data shown in Table E-2 were calculated.

TABLE E-1. STORAGE TANK INPUT DATA FOR AN ACRYLONITRILE PLANT (UNCONTROLLED EMISSIONS)

	Tank identification			
Input information	Product acrylonitrile	Product acrylonitrile	Off-specification acrylonitrile	Crude acrylonitrile
Number of tanks	2	3	1	2
Production capacity, tons/yr	100,000	100,000	100,000	100,000
Ambient temperature, °F	64	64	64	64
Average temperature change, °F	19	19	19	19
Molecular weight, lb/lb-mole	53	53	53	53
Liquid density, lb/gal	6.76	6.76	6.76	6.76
Vapor pressure, psia	1.78	1.78	1.78	1.78
Bulk temperature, °F	69	69	69	69
Tank diameter, ft	16	40	21	28
Tank outage, ft	10	25	25	25
Paint factor	1.0	1.0	1.0	1.0
Diameter factor	0.77	1.0	0.92	0.48
Turnover factor	0.25	1.0	1.0	1.0
Number of turnovers per year	450	25	5	2
Tank volume, bbl	715	10,714	2,976	5,476

TABLE E-2. STORAGE TANK EMISSIONS SUMMARY (UNCONTROLLED EMISSIONS)

Material stored	Capacity, gal	Losses gal/yr	Losses lb/yr	Emission factor, g/kg
Product acrylonitrile	30,000	1,350	9,100	0.046
Product acrylonitrile	30,000	1,350	9,100	0.046
Product acrylonitrile	450,000	5,950	40,200	0.2
Product acrylonitrile	450,000	5,950	40,200	0.2
Product acrylonitrile	450,000	5,950	40,200	0.2
Off-specification acrylonitrile	125,000	870	5,800	0.03
Crude acrylonitrile	230,000	1,300	8,850	0.04
Crude acrylonitrile	230,000	1,300	8,850	0.04

APPENDIX F

FUGITIVE EMISSION LOSS CALCULATIONS

Fugitive emission losses from a representative acrylonitrile plant were calculated by identifying the fugitive emission points and calculating the emissions using emission factors contained in the Air Pollution Engineering Manual.[12] The fugitive emission points consist of pressure relief valves and mechanical pump seals. Emission factors are: 3.5 lb/day per valve for pressure relief valves, and 20 lb/10^3 bbl of pumped liquid for mechanical seals.[12] Individual emission points, materials emitted, emission rates, and emission factors (g/kg acrylonitrile produced) are presented in Table F-1. The basis for the information contained in the table is the material balance presented in Section III.

TABLE F-1. FUGITIVE EMISSION LOSSES FOR A REPRESENTATIVE ACRYLONITRILE PLANT

Emission point (by stream name)	Material emitted	Emission rate, kg/hr	Emission factor, μg/kg
Pressure relief valves			
Propylene storage	Propylene	0.066	6
	Propane	0.0066	0.6
Ammonia storage	Ammonia	0.066	6
Pump seals			
Absorber column bottoms	Acrylonitrile	0.77	70
	Acetonitrile	0.09	8
Crude acrylonitrile (to storage)	Acrylonitrile	0.77	70
Crude acrylonitrile (to purification)	Acrylonitrile	0.77	70
Crude acetonitrile (to storage)	Acetonitrile	0.09	8
Crude acetonitrile (to incineration)	Acetonitrile	0.09	8
Light ends column bottoms	Acrylonitrile	0.77	70
Product acrylonitrile (to storage)	Acrylonitrile	0.77	70
Product acrylonitrile (to loading rack)	Acrylonitrile	0.77	70

APPENDIX G

PRODUCT TRANSPORT LOADING FACILITY EMISSION FACTORS

Atmospheric emissions from the product transport loading facility were calculated using emission factors presented in the Air Pollution Engineering Manual.[12] The emission factor for controlled losses is 2 $lb/10^3$ bbl of material shipped.[12] This is equivalent to 6.5 mg/kg of product for a representative acrylonitrile plant. (From Reference 12 and personal communication, T. W. Hughes of Monsanto Research Corporation and W. Fitzgibbons of The Standard Oil Company, June 23, 1975.)

APPENDIX H

DERIVATION OF SOURCE SEVERITY EQUATIONS[a]

1. SUMMARY OF MAXIMUM SEVERITY EQUATIONS

The maximum severity of pollutants may be calculated using the mass emission rate, Q, the height of the emissions, H, and the ambient air quality standard, AAQS. The equations summarized in Table H-1 are developed in detail in this appendix.

TABLE H-1. POLLUTANT SEVERITY EQUATIONS FOR ELEVATED SOURCES

Pollutant	Severity equation
Particulates	$S = \frac{70\ Q}{H^2}$
SO_x	$S = \frac{50\ Q}{H^2}$
NO_x	$S = \frac{315\ Q}{H^{2.1}}$
Hydrocarbons	$S = \frac{162\ Q}{H^2}$
CO	$S = \frac{0.78\ Q}{H^2}$
Others	$S = \frac{5.5\ Q}{TLV \cdot H^2}$

2. DERIVATION OF χ_{max} FOR USE WITH U.S. AVERAGE CONDITIONS

The most widely accepted formula for predicting downwind ground level concentrations from a point source is:[21]

---

[a] This Appendix was prepared by T. R. Blackwood and E. C. Eimutis of Monsanto Research Corporation, Dayton, Ohio.

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$$\chi = \frac{Q}{\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(H-1)}$$

where χ = downwind ground level concentration at reference coordinate x and y with emission height of H, g/m^3

Q = mass emission rate, g/s

σ_y = standard deviation of horizontal dispersion, m

σ_z = standard deviation of vertical dispersion, m

u = wind speed, m/s

y = horizontal distance from centerline of dispersion, m

H = height of emission release, m

x = downwind emission dispersion distance from source of emission release, m

π = 3.1416

We assume that χ_{max} occurs when $x >> 0$ and $y = 0$. For a given stability class, standard deviations of horizontal and vertical dispersion have often been expressed as a function of downwind distance by power law relationships as follows:[33]

$$\sigma_y = ax^b \qquad \text{(H-2)}$$

$$\sigma_z = cx^d + f \qquad \text{(H-3)}$$

Values for a, b, c, d, and f are given in Tables H-2[34] and H-3. Substituting these general equations into Equation H-1 yields:

$$\chi = \frac{Q}{ac\pi ux^{b+d} + a\pi ufx^b} \exp\left[-\frac{H^2}{2(cx^d + f)^2}\right] \qquad \text{(H-4)}$$

Assuming that χ_{max} occurs at $x < 100$ m and the stability class is C, then $f = 0$ and Equation H-4 becomes:

$$\chi = \frac{Q}{ac\pi ux^{b+d}} \exp\left[\frac{-H^2}{2c^2x^{2d}}\right] \qquad \text{(H-5)}$$

---

[33] Martin, D. O., and J. A. Tikvart. A General Atmospheric Diffusion Model for Estimating the Effects on Air Quality of One or More Sources. Presented at the 61st Annual Meeting of the Air Pollution Control Association, St. Paul, Minnesota, June 23-27, 1968. 18 pp.

[34] Tadmor, J., and Y. Gur. Analytical Expressions for the Vertical and Lateral Dispersion Coefficients in Atmospheric Diffusion. Atmospheric Environment, 3(6):688-689, November 1969.

TABLE H-2. VALUES OF a FOR THE COMPUTATION OF σ_y[a,34]

Stability class	a
A	0.3658
B	0.2751
C	0.2089
D	0.1471
E	0.1046
F	0.0722

[a] For Equation H-2: $\sigma_y = ax^b$

where x = downwind distance
b = 0.9031

TABLE H-3. VALUES OF THE CONSTANTS USED TO ESTIMATE VERTICAL DISPERSION[a,21]

Usable range	Stability class	Coefficient		
		c_1	d_1	f_1
>1,000 m	A	0.00024	2.094	9.6
	B	0.055	1.098	2.0
	C	0.113	0.911	0.0
	D	1.26	0.516	-13
	E	6.73	0.305	-34
	F	18.05	0.18	-48.6
		c_2	d_2	f_2
100 to 1,000 m	A	0.0015	1.941	9.27
	B	0.028	1.149	3.3
	C	0.113	0.911	0.0
	D	0.222	0.725	-1.7
	E	0.211	0.678	-1.3
	F	0.086	0.74	-0.35
		c_3	d_3	f_3
<100 m	A	0.192	0.936	0
	B	0.156	0.922	0
	C	0.116	0.905	0
	D	0.079	0.881	0
	E	0.063	0.871	0
	F	0.053	0.814	0

[a] For Equation H-3: $\sigma_z = cx^d + f$

For convenience, let:

$$A_R = \frac{Q}{ac\pi u} \text{ and } B_R = \frac{-H^2}{2c^2}$$

so that Equation H-5 reduces to:

$$\chi = A_R x^{-(b+d)} \exp\left[\frac{B_R}{x^{2d}}\right] \qquad \text{(H-6)}$$

Taking the first derivative of Equation H-6

$$\frac{d\chi}{dx} = A_R \left\{ x^{-b-d}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-2dB_R x^{-2d-1}\right) + \exp\left[B_R x^{-2d}\right]\left(-b-d\right)x^{-b-d-1} \right\} \qquad \text{(H-7)}$$

and setting this equal to zero (to determine the roots which give the minimum and maximum conditions of χ with respect to x) yields:

$$\frac{d\chi}{dx} = 0 = A_R x^{-b-d-1}\left(\exp\left[B_R x^{-2d}\right]\right)\left(-2dB_R x^{-2d} - b - d\right) \qquad \text{(H-8)}$$

Since we define that $x \neq 0$ or ∞ at χ_{max}, the following expression must be equal to 0:

$$-2dB_R x^{-2d} - d - b = 0 \qquad \text{(H-9)}$$

or

$$(b+d)x^{2d} = -2dB_R \qquad \text{(H-10)}$$

or

$$x^{2d} = \frac{-2dB_R}{b+d} = \frac{2d\ H^2}{2c^2(b+d)} \qquad \text{(H-11)}$$

or

$$x^{2d} = \frac{d\ H^2}{c^2(b+d)} \qquad \text{(H-12)}$$

Hence

$$x = \left(\frac{d\ H^2}{c^2(b+d)}\right)^{1/2d} \text{ at } \chi_{max} \qquad \text{(H-13)}$$

Thus Equation H-2 and H-3 (at f = 0) become:

$$\sigma_y = a\left(\frac{d\ H^2}{c^2\,(d+b)}\right)^{b/2d} \qquad \text{(H-14)}$$

$$\sigma_z = c\left(\frac{d\ H^2}{c^2\,(b+d)}\right)^{d/2d} = \left(\frac{d\ H^2}{b+d}\right)^{1/2} \qquad \text{(H-15)}$$

The maximum will be determined for U.S. average conditions of stability. According to Gifford,[35] this is when $\sigma_y = \sigma_z$. Since $b = 0.9031$, and upon inspection of Table H-2[34] under U.S. average conditions, $\sigma_y = \sigma_z$, it can be seen that $0.881 \leq d \leq 0.905$ (class C stability[a]). Thus, it can be assumed that b is nearly equal to d in Equations H-14 and H-15 or:

$$\sigma_z = \frac{H}{\sqrt{2}} \qquad \text{(H-16)}$$

and

$$\sigma_y = \frac{aH}{c\sqrt{2}} \qquad \text{(H-17)}$$

Under U.S. average conditions, $\sigma_y = \sigma_z$ and $a \cong c$ if $b \cong d$ and $f = 0$ (between class C and D, but closer to belonging in class C).

Then

$$\sigma_y = \frac{H}{\sqrt{2}} \qquad \text{(H-18)}$$

Substituting for σ_y from Equation H-18 and for σ_z from Equation H-16 into Equation H-1 and letting $y = 0$:

---

[a] The values given in Table H-3 are mean values for stability class. Class C stability describes these coefficients and exponents, only within about a factor of two.

- - - - - - - - - - -

[35] Gifford, F. A., Jr. An Outline of Theories of Diffusion in the Lower Layers of the Atmosphere. In: Meteorology and Atomic Energy 1968, Chapter 3, D. A. Slade, ed. Publication No. TID-24190, U.S. Atomic Energy Commission Technical Information Center, Oak Ridge, Tennessee, July 1968. p. 113.

$$\chi_{max} = \frac{2\ Q}{\pi u H^2} \exp\left[-\frac{1}{2}\left(\frac{H\sqrt{2}}{H}\right)^2\right] \qquad \text{(H-19)}$$

or

$$\chi_{max} = \frac{2\ Q}{\pi e u H^2} \qquad \text{(H-20)}$$

3. DEVELOPMENT OF SOURCE SEVERITY EQUATIONS

Source severity, S, has been defined as follows:

$$S = \frac{\overline{\chi}_{max}}{AAQS} \text{ and } S = \frac{\overline{\chi}_{max}}{F} \qquad \text{(H-21)}$$

where $\overline{\chi}_{max}$ = time-averaged maximum ground level concentration
AAQS = ambient air quality standard
F = TLV • 8/24 • 1/100

Values of $\overline{\chi}_{max}$ are found from the following equation:

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{t_0}{t}\right)^{0.17} \qquad \text{(H-22)}$$

where t_0 is the "instantaneous" (i.e., 3-minute) averaging time and t is the averaging time used for the ambient air quality standard as shown in Table H-4.

a. CO Severity

The primary standard for CO is reported for a 1-hr averaging time. Therefore,

$$t = 60 \text{ min}$$

$$t_0 = 3 \text{ min}$$

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(H-23)}$$

$$= \frac{2\ Q}{\pi e u H^2}\left(\frac{3}{60}\right)^{0.17} \qquad \text{(H-24)}$$

$$= \frac{2\ Q}{(3.14)(2.72)(4.5)H^2}\ (0.6) \qquad \text{(H-25)}$$

$$= \frac{0.052\ Q}{H^2}\ (0.6) \qquad \text{(H-26)}$$

TABLE H-4. SUMMARY OF NATIONAL AMBIENT AIR QUALITY STANDARDS[36]

Pollutant	Averaging time, hr	Primary standards, µg/m^3 (ppm)	Secondary standards, µg/m^3
Particulate	Annual (geometric mean)	75	60[a]
	24[b]	260	150
Sulfur oxides	Annual (arithmetic mean)	80 (0.03)	60 (0.02)
	24[b]	365 (0.14)	260[c] (0.1)
	3[b]	None	1,300 (0.5)
Carbon monoxide	8[b]	10,000 (9)	None
	1[b]	40,000 (35)	(Same as primary)
Nitrogen dioxide	Annual (arithmetic mean)	100 (0.05)	(Same as primary)
Photochemical oxidants	1[b]	160 (0.08)	(Same as primary)
Hydrocarbons (nonmethane)	3 (6 a.m. to 9 a.m.)	160[d] (0.24)	(Same as primary)

[a] The secondary annual standard (60 µg/m^3) is a guide for assessing implementation plants to achieve the 24-hr secondary standard.

[b] Not to be exceeded more than once per year.

[c] The secondary annual standard (260 µg/m^3) is a guide for assessing implementation plans to achieve the annual standard.

[d] Recommended guideline.

$$\bar{X}_{max} = \frac{3.12 \times 10^{-2}\ Q}{H^2} \qquad \text{(H-27)}$$

Substituting the primary standard for CO (0.04 g/m^3) into the equation for S then gives:

$$S = \frac{\bar{X}_{max}}{AAQS} = \frac{3.12 \times 10^{-2}\ Q}{0.04\ H^2} \qquad \text{(H-28)}$$

---

[36] Code of Federal Regulations, Title 42 - Public Health, Chapter IV - Environmental Protection Agency, Part 410 - National Primary and Secondary Ambient Air Quality Standards, April 28, 1971. 16 pp.

or

$$S_{CO} = \frac{0.78\ Q}{H^2} \qquad \text{(H-29)}$$

b. Hydrocarbon Severity

For nonmethane hydrocarbons, a 3-hr averaging time is used.

$$t = 180\ \text{min}$$

$$\bar{X}_{max} = X_{max}\left(\frac{3}{180}\right)^{0.17} \qquad \text{(H-30)}$$

$$= 0.5\ X_{max} \qquad \text{(H-31)}$$

$$= \frac{(0.5)(0.052)\ Q}{H^2} \qquad \text{(H-32)}$$

$$\bar{X}_{max} = \frac{0.026\ Q}{H^2} \qquad \text{(H-33)}$$

For nonmethane hydrocarbons, the concentration of 1.6×10^{-4} g/m^3 has been issued as a guide for achieving oxidant standards. Therefore

$$S = \frac{\bar{X}_{max}}{\text{AAQS}} = \frac{0.026\ Q}{1.6 \times 10^{-4}\ H^2} \qquad \text{(H-34)}$$

or

$$S_{HC} = \frac{162.5\ Q}{H^2} \qquad \text{(H-35)}$$

c. Particulate Severity

The primary standard for particulate is reported for a 24-hr averaging time.

$$\bar{X}_{max} = X_{max}\left(\frac{3}{1,440}\right)^{0.17} \qquad \text{(H-36)}$$

$$= \frac{0.052\ Q}{H^2}\ (0.35) \qquad \text{(H-37)}$$

$$\bar{X}_{max} = \frac{0.0182\ Q}{H^2} \qquad \text{(H-38)}$$

For particulates, AAQS = 2.6×10^{-4} g/m^3. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{2.6 \times 10^{-4}\ H^2} \qquad \text{(H-39)}$$

$$S_P = \frac{70\ Q}{H^2} \qquad \text{(H-40)}$$

d. SO_2 Severity

The primary standard for SO_x is reported for a 24-hr averaging time. Using t = 1,440 minutes and proceeding as before:

$$\bar{\chi}_{max} = \frac{0.0182\ Q}{H^2} \qquad \text{(H-41)}$$

For SO_2, AAQS = 3.65×10^{-4} g/m^3. Therefore

$$S = \frac{\bar{\chi}_{max}}{AAQS} = \frac{0.0182\ Q}{3.65 \times 10^{-4}\ H^2} \qquad \text{(H-42)}$$

or

$$S_{SO_2} = \frac{50\ Q}{H^2} \qquad \text{(H-43)}$$

e. NO_2 Severity

Since NO_2 has a primary standard with a 1-yr averaging time, the χ_{max} correction equation cannot be used. Alternatively, the following equation is used:

$$\bar{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(H-44)}$$

A difficulty arises, however, because a distance, x, from emission point to receptor, is included and hence, the following rationale is used:

Equation H-20 is valid for neutral conditions or when $\sigma_z \cong \sigma_y$. This maximum occurs when

$$H \simeq \sqrt{2}\sigma_z$$

and since, under these conditions,

$$\sigma_z = ax^b$$

then the distance x_{max} where the maximum concentration occurs is:

$$x_{max} = \left(\frac{H}{\sqrt{2}a}\right)^{1/b} \qquad \text{(H-45)}$$

For Class C conditions, a = 0.113 and b = 0.911. Substituting these values into Equation H-45 yields:

$$x_{max} = \frac{H^{1.098}}{0.16} = 7.5\ H^{1.098} \qquad \text{(H-46)}$$

Since

$$\sigma_z = 0.113\ x_{max}{}^{0.911}$$

and

$$u = 4.5\ \text{m/s}$$

and letting $x = x_{max}$, Equation H-44 becomes:

$$\bar{\chi}_{max} = \frac{4\ Q}{x_{max}{}^{1.911}} \quad \exp\left[-\ \frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(H-47)}$$

In Equation H-47, the factor

$$\frac{4\ Q}{x_{max}{}^{1.911}} = \frac{4\ Q}{(7.5\ H^{1.098})^{1.911}} \qquad \text{(H-48)}$$

Therefore,

$$\bar{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \quad \exp\left[-\ \frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(H-49)}$$

As noted above,

$$\sigma_z = 0.113\ x^{0.911} \qquad \text{(H-50)}$$

Substitution for x yields

$$\sigma_z = 0.113\ (7.5\ H^{1.1})^{0.911} \qquad \text{(H-51)}$$

$$\sigma_z = 0.71\ H \qquad \text{(H-52)}$$

Therefore:

$$\overline{\chi}_{max} = \frac{0.085\ Q}{H^{2.1}} \exp\left[-\frac{1}{2}\left(\frac{H}{0.71\ H}\right)^2\right] \qquad \text{(H-53)}$$

$$= \frac{0.085\ Q}{H^{2.1}} (0.371) \qquad \text{(H-54)}$$

or

$$\overline{\chi}_{max} = \frac{3.15 \times 10^{-2}\ Q}{H^{2.1}} \qquad \text{(H-55)}$$

Since the NO_2 standard is 1.0×10^{-4} g/m^3, the NO_2 severity equation is:

$$S_{NO_2} = \frac{3.15 \times 10^{-2}\ Q}{1 \times 10^{-4}\ H^{2.1}} \qquad \text{(H-56)}$$

or

$$S_{NO_2} = \frac{315\ Q}{H^{2.1}} \qquad \text{(H-57)}$$

f. Noncriteria Emissions

The value of $\overline{\chi}$ may be derived from χ_{max}, an undefined "short-term" concentration. An approximation for longer term concentration may be made as follows:

For a 24-hr time period,

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{t_o}{t}\right)^{0.17} \qquad \text{(H-22)}$$

$$\overline{\chi}_{max} = \chi_{max}\left(\frac{3\ \text{min}}{1,440\ \text{min}}\right)^{0.17} \qquad \text{(H-58)}$$

$$\overline{\chi}_{max} = \chi_{max}(0.35) \qquad \text{(H-59)}$$

Since the source severity is defined and derived from TLV values as follows:

$$F = (\text{TLV})\left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \qquad \text{(H-60)}$$

$$F = (0.0033)\ \text{TLV} \qquad \text{(H-61)}$$

then the source severity, S, is defined as

$$S = \frac{\overline{\chi}_{max}}{F} = \frac{(0.35)\chi_{max}}{(3.33 \times 10^{-3})\ TLV} \quad \text{(H-62)}$$

$$S = \frac{105\ \chi_{max}}{TLV} \quad \text{(H-63)}$$

If a weekly averaging period is used, then

$$\overline{\chi} = \chi_{max}\left(\frac{3}{10,080}\right)^{0.17} \quad \text{(H-64)}$$

or

$$\overline{\chi} = (0.25)\chi_{max} \quad \text{(H-65)}$$

and

$$F = (TLV)\left(\frac{40}{168}\right)\left(\frac{1}{100}\right) \quad \text{(H-66)}$$

$$F = (2.38 \times 10^{-3})TLV \quad \text{(H-67)}$$

and the source severity, S, is

$$S = \frac{\overline{\chi}_{max}}{F} = \frac{(0.25)\chi_{max}}{(2.38 \times 10^{-3})\ TLV} \quad \text{(H-68)}$$

or

$$S = \frac{105\ \chi_{max}}{TLV} \quad \text{(H-69)}$$

which is entirely consistent, since the TLV is being corrected for a different exposure period.

Therefore, the severity can be derived from χ_{max} directly without regard to averaging time for noncriteria emissions. Thus, combining Equations H-69 and H-20, for elevated source, gives:

$$S = \frac{5.5\ Q}{TLV \cdot H^2} \quad \text{(H-70)}$$

4. AFFECTED POPULATION CALCULATION

Another form of the plume dispersion equation is needed to calculate the affected population since the population is assumed to be distributed uniformly around the source. If the wind directions are taken to 16 points and it is assumed that the wind tions are taken to 16 points and it is assumed that the wind directions within each sector are distributed randomly over a period of a month or a season, it can be assumed that the effluent is uniformly distributed in the horizontal within the sector. The appropriate equation for average concentration, $\overline{\chi}$, in g/m^3 is then (for 100 m $\leq x \leq$ 1,000 m and stability class C):[20]

$$\overline{\chi} = \frac{2.03\ Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad \text{(H-71)}$$

To find the distances at which $\overline{\chi}$/AAQS = 1.0, roots are determined for the following equation:

$$\frac{2.03}{(\text{AAQS})} \frac{Q}{\sigma_z u x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] = 1.0 \qquad \text{(H-72)}$$

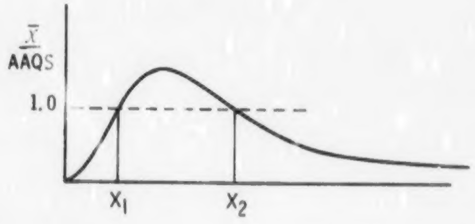
keeping in mind that:

$$\sigma_z = ax^b + c$$

where a, b, and c are functions of atmospheric stability and are assumed to be selected for stability Class C.

Since Equation H-72 is a transcendental equation, the roots are found by an iterative technique using the computer.

For a specified emission from a typical source, $\overline{\chi}$/AAQS as a function of distance might look as follows:



The affected population is contained in the area

$$A = \pi(x_2{}^2 - x_1{}^2) \qquad \text{(H-73)}$$

If the affected population density is D_p, the total affected population, P', is

$$P' = D_p A \text{ (persons)} \qquad \text{(H-74)}$$

APPENDIX I

AFFECTED POPULATION CALCULATIONS

The affected population was calculated using the procedure outlined in Section 4, Appendix H. Input data and results are shown in Table I-1 for the absorber vent, fugitive emissions, product transport loading, storage tanks, incinerator, flare stack and deep well pond. In all calculations, uncontrolled emissions were assumed. When using emissions control on the absorber vent, the source severity is less than 1.0, hence the affected population is zero.

TABLE I-1. AFFECTED POPULATION CALCULATIONS

	Absorber vent (uncontrolled emissions)									
	Data input						Data output			
Component	Emission rate, g/s	Emission height, m	TLV, g/m^3	Hazard factor,[a] g/m^3	Wind speed, m/s	Population density, persons/km^2	Root x_1, km	Root x_2, km	Affected area, km^2	Affected population, persons
Carbon monoxide	353	62.8	NA[b]	0.040	4.5	402	0	0	0	0
Hydrocarbons	255	62.8	NA	0.00016	4.5	402	0.299	3.53	33.0	15,700
Methane	2.99	62.8	0.714	0.00238	4.5	402	0	0	0	0
Ethane	8.59	62.8	1.34	0.00447	4.5	402	0	0	0	0
Ethylene	11.4	62.8	1.25	0.00418	4.5	402	0	0	0	0
Propane and propylene	250	62.8	1.96	0.00640	4.5	402	0	0	0	0
Butene	1.78	62.8	2.5	0.00833	4.5	402	0	0	0	0
Toluene	0.29	62.8	0.375	0.00125	4.5	402	0	0	0	0
Acrylonitrile	0.17	62.8	0.045	0.00015	4.5	402	0	0	0	0
Benzene	0.65	62.8	0.003	0.00010	4.5	402	0	0	0	0
Acetonitrile	2.78	62.8	0.070	0.00023	4.5	402	0	0	0	0
Hydrogen cyanide	1.23	62.8	0.011	0.000037	4.5	402	0	0	0	0
Propionaldehyde	0.03	62.8	0.003	0.000010	4.5	402	0	0	0	0
Furan	2.08	62.8	0.020	0.000067	4.5	402	0	0	0	0
Allyl alcohol	0.11	62.8	0.005	0.000017	4.5	402	0	0	0	0
	Fugitive emissions (uncontrolled emissions)									
Hydrocarbons	0.002	9.1	NA	0.000160	4.5	402	0	0	0	0
Acrylonitrile	0.0019	9.1	0.045	0.000150	4.5	402	0	0	0	0
Acetonitrile	0.0001	9.1	0.070	0.000233	4.5	402	0	0	0	0
Propane and propylene	0.00002	9.1	1.96	0.0064	4.5	402	0	0	0	0
Ammonia	0.00002	9.1	0.018	0.00006	4.5	402	0	0	0	0
	Product transport loading facility (uncontrolled emissions)									
Acrylonitrile	0.029	9.1	0.045	0.000150	4.5	402	0	0	0	0
	Storage tanks (uncontrolled emissions)									
Acrylonitrile[c]	0.206	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[c]	0.206	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[d]	0.9	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[d]	0.9	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[d]	0.9	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[e]	0.13	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[f]	0.13	15.2	0.045	0.00015	4.5	402	0	0	0	0
Acrylonitrile[f]	0.13	15.2	0.045	0.00015	4.5	402	0	0	0	0
	Incinerator (uncontrolled emissions)									
Carbon monoxide	0.0179	33.5	NA	0.040	4.5	402	0	0	0	0
Hydrocarbons	0.056	33.5	NA	0.000160	4.5	402	0	0	0	0
Nitrogen oxides	1.4	33.5	NA	0.000100	4.5	402	0	0	0	0
Sulfur oxides	0.0789	33.5	NA	0.000365	4.5	402	0	0	0	0
Methane	0.0103	33.5	0.714	0.0024	4.5	402	0	0	0	0
Hydrogen cyanide	0.154	33.5	0.011	0.000037	4.5	402	0	0	0	0
	Flare stack (uncontrolled emissions)									
Hydrocarbons	1.83	62.9	NA	0.000160	4.5	402	0	0	0	0
Nitrogen oxides	0.04	62.9	NA	0.000100	4.5	402	0	0	0	0
Propane and propylene	0.099	62.9	1.96	0.00640	4.5	402	0	0	0	0
Acrylonitrile	0.17	62.9	0.045	0.000150	4.5	402	0	0	0	0
Hydrogen cyanide	1.6	62.9	0.011	0.000037	4.5	402	0	0	0	0
	Deep well pond (uncontrolled emissions)									
Hydrocarbons	63	9.1	NA	0.000160	4.5	402	0.029	1.2	3.94	9,100
Fumaronitrile	0.16	9.1	_[g]	_[g]	4.5	402	0	0	0	0
Pyridine	23	9.1	0.015	0.00005	4.5	402	0.02	1.6	27	11,000

[a] Hazard factor = primary ambient air quality standard for criteria pollutants
= TLV • 8/24 • 1/100 for noncriteria pollutants.

[b] Not applicable. [c] Rundown tank.

[d] Field storage. [e] Off-specification acrylonitrile. [f] Crude acrylonitrile. [g] Not applicable; no TLV has been established.

APPENDIX J

SAMPLING AND ANALYSIS METHODS USED AT ACRYLONITRILE PLANTS

1. TEST SITE PREPARATIONS REQUIRED

Field sampling at the acrylonitrile plants did not require test site modifications. All of the emissions of concern in these plants are gaseous materials, i.e., SO_2, NO_x, HCN, CO, acetonitrile, acrylonitrile and C_2 and C_3 hydrocarbons. Therefore, isokinetic sampling was not necessary. The velocity, pressure, and temperature of the absorber and incinerator stacks are continuously monitored since the acrylonitrile process is designed for 100% remote control of operations. Control room data were employed in conjunction with the measurement of sample volume to calculate emission factors after sampling had been completed. The plant monitors were calibrated before the sampling program to assure accuracy.

Stainless steel sample lines are installed at the facilities and are accessible from a platform. The line at the absorber vent samples gases between the absorber and the pressure control valve. Since this line is under positive pressure (35 kPa gage) it was purged before sampling and no pump was required during sampling. The temperature at the absorber vent was 49°C and the line was not heated. To prevent condensation of the water-saturated stream it was necessary to heat this sampling line to 50°C during the sampling with an existing steam tracing on the line. Sketches showing the existing sampling locations at Plant A and Plant B are presented in Figures J-1 and J-2.

At the incinerator, stainless steel sampling lines lead to a ground level sampling location. The temperature of the incinerated gases is 870°C and required cooling to 540°C before introduction into the sampling train to prevent the glassware from melting. This was achieved by air cooling of the sampling line.

2. SAMPLING METHODS AND EQUIPMENT

a. Nitrogen and Sulfur Oxides

Method 6 was employed for SO_2 determination and Method 7 was used for sampling and analysis of NO_x. Since these methods are

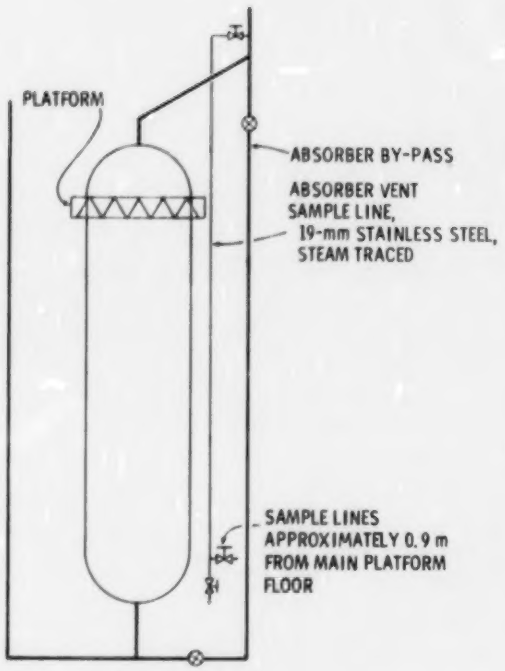

PLATFORM
ABSORBER BY-PASS
ABSORBER VENT SAMPLE LINE, 19-mm STAINLESS STEEL, STEAM TRACED
SAMPLE LINES APPROXIMATELY 0.9 m FROM MAIN PLATFORM FLOOR

Figure J-1. Available sampling lines at Plant A.

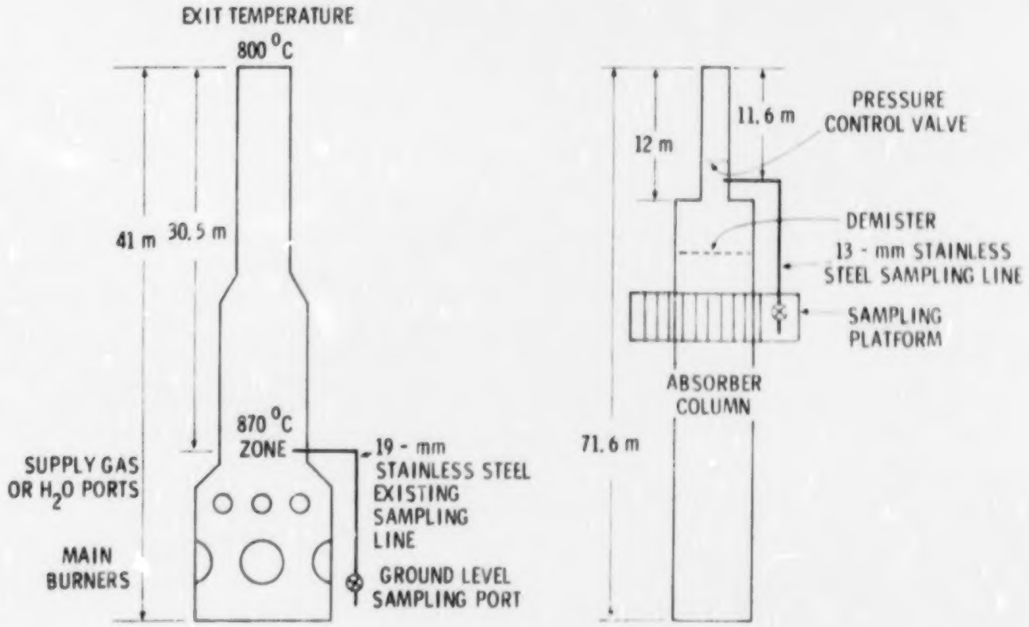

EXIT TEMPERATURE
800 °C
41 m
30.5 m
870 °C ZONE
SUPPLY GAS OR H2O PORTS
MAIN BURNERS
19 - mm STAINLESS STEEL EXISTING SAMPLING LINE
GROUND LEVEL SAMPLING PORT
12 m
11.6 m
PRESSURE CONTROL VALVE
DEMISTER
13 - mm STAINLESS STEEL SAMPLING LINE
SAMPLING PLATFORM
ABSORBER COLUMN
71.6 m

Figure J-2. Available sampling lines at Plant B.

described in the Federal Register[37,38] they will not be discussed here. Measurements were made under steady state conditions.

b. Hydrogen Cyanide, Acrylonitrile and Acetonitrile

A separate absorption train was employed for sampling of hydrogen cyanide, acrylonitrile and acetonitrile. The sampling train is presented schematically in Figure J-3.

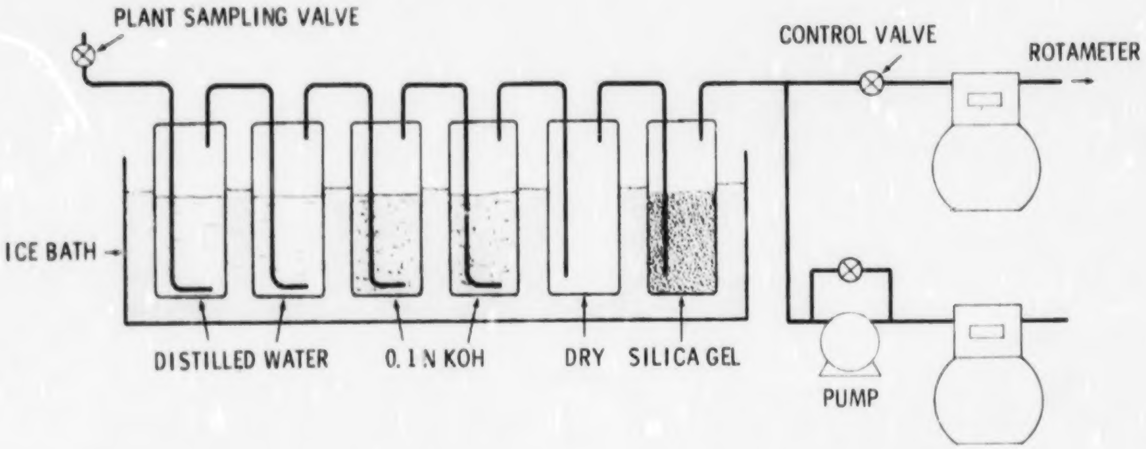


Figure J-3. Sampling train for acrylonitrile, acetonitrile and hydrogen cyanide emissions.

The train is an all-glass system which was connected to the sampling line with Teflon tubing. It consists of four bubblers and two impinger units all maintained at 0°C in an ice bath. The first two units contained 0.0001 m^3 of distilled water for absorption of acrylonitrile and acetonitrile. The next two units contained 0.0001 m^3 of 0.1N KOH for absorption of hydrogen cyanide. The first four impingers were fitted with fritted-glass bubblers. These impingers were followed by a dry impinger and a silica gel impinger. The last impinger was connected to a dry test meter (Type A2-110 American Meter Co.).

Sampling rates were adjusted to 0.001 m^3/min and sampling was continued for a period of 30 minutes. After completion of the sampling run, the train was disconnected from the gas sampling

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[37] Determination of Sulfur Dioxide Emissions from Stationary Sources - Method 6. Federal Register, 36(24):24882-24891, 1971.

[38] Determination of Nitrogen Oxide Emissions from Stationary Sources - Method 7. Federal Register, 36(24):24891-24893, 1971.

line and the impinger contents transferred to clean sample bottles. Each impinger and the connecting tubing was rinsed three times with fresh portions of the collection liquid. All samples were returned to MRC's Dayton Laboratory for analysis.

Preliminary experiments were conducted at the Dayton Laboratory to test the feasibility of collecting acrylonitrile and acetonitrile in distilled water. The sample generation and collection system is presented in Figure J-4. An A.I.D. Model 309 Calibration System was employed to generate the nitriles via a diffusion tube filled with 2.5 x 10^{-6} m^3 of the liquid. Nitrogen gas was admitted into the mixing chamber and this stream containing the nitrile vapor underwent secondary dilution via a metered nitrogen flow admitted at a 3-way stopcock just upstream of the sampling train. The method of sample generation does not represent a primary standard since the nitrile vapor composition can only be estimated due to uncertainties in the diffusion coefficients and their temperature dependence. An indication of the collection efficiency is demonstrated by the data presented in Table J-1 where the distributions of the nitriles between the three impingers are presented for two estimated concentration levels.

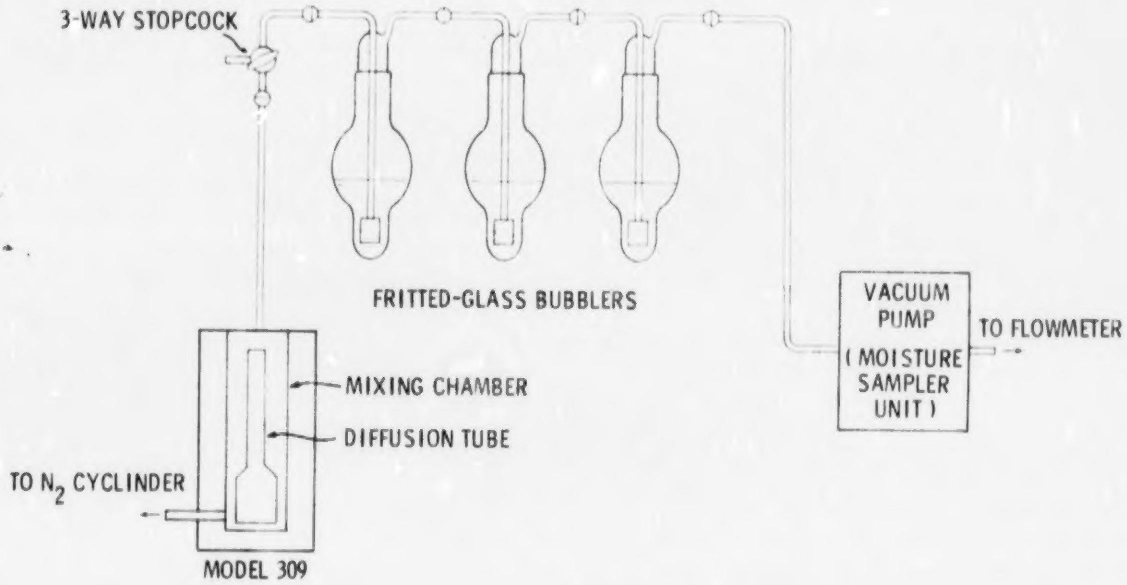

Figure J-4. Laboratory sample generation and collection system for acrylonitrile and acetonitrile.

TABLE J-1. DISTRIBUTION OF ACRYLONITRILE AND ACETONITRILE IN THREE TANDEM DISTILLED WATER IMPINGERS

Sample	Estimated gaseous concentration, ppm v/v	Percent of total nitrile collected in bubblers		
		1st	2nd	3rd
Acrylonitrile	157	80	18	2
Acrylonitrile	0.65	84	16	0
Acetonitrile	64	95	5	0
Acetonitrile	0.68	100	0	0

The acidic nature of hydrogen cyanide assures quantitative collection (99.5+%) in 0.1N KOH.

The analyses of the impinger contents presented in Table J-1 were conducted employing the gas chromatographic-flame ionization method described in Section 3 of this appendix.

This sampling train was used to collect acrylonitrile, acetonitrile, and hydrogen cyanide from the absorber and the incinerator.

c. Carbon Monoxide, Propane, Propylene and Other Organic Species

Carbon monoxide, propane, and propylene from the absorber vent were sampled using Tedlar bags. Background measurements taken before sampling indicated that the bags contained <10 vppm of CO and <1 ppm of hydrocarbons. Prior to sampling, the bags were evacuated to <0.1 mm Hg pressure. A Teflon tube connected the bag to the sampling line. The stopcock on each bag was closed and taped and the bags returned to the laboratory for analysis.

d. Acrylonitrile Settling Pond Emissions

Since there are no data describing emissions from the acrylonitrile settling pond, an open source sampling effort was used. The settling ponds are covered by an oil film to moderate evaporation of materials from the pond. The species of interest in this case were assumed to be acrylonitrile and acetonitrile from the plant process, and hydrocarbons from the oil film.

Since these emissions were diluted in an ambient air matrix, an experimental ambient air sampling system was employed involving sampling through a porous polymer packed tube.[39] The polymers are chromatographic substrates which do not absorb water vapor but absorb hydrocarbon species such as higher ($>C_7$) hydrocarbons, acrylonitrile and acetonitrile.

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[39] Mienire, J. P., and M. W. Dietrich. Determination of Trace Organics in Air and Water. Journal of Chromatographic Science, 11(11):559-570, 1973.

The sampling system as shown in Figure J-5 consisted of a 6.4 mm or 9.5 mm stainless steel tube 150 mm long packed with porous polymer bead material. This sampling tube was attached to a pump (Model MP-155 Metal Bellows Corp.), a rotometer with valve (Dwyer 0-0.14 m^3/hr), and a gas meter (Type AI-110 American Meter Co.). The pump was required due to pressure drop caused by the packing in the tube.

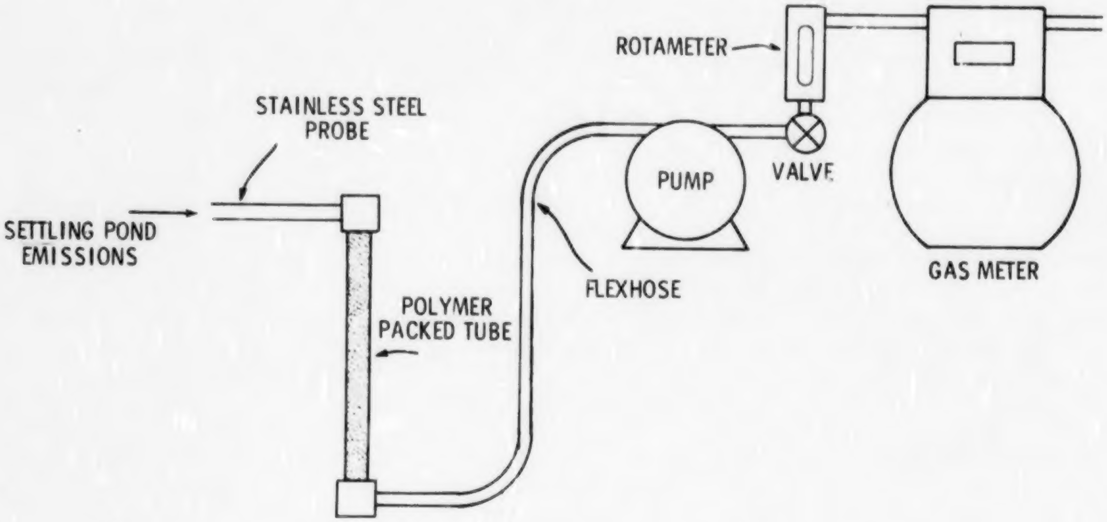

Figure J-5. Porous polymer tube sampling train.

In operation the tube was connected to the sample line and the pump turned on. Samples were collected over 5 to 30 minute periods and the barometric pressure, meter pressure and temperature and gas volume were recorded. The hydrocarbon and organic emissions were adsorbed on the packing and polar materials such as water vapor pass through. After sampling, the tube was removed from the train and capped with stainless steel tube closures.

3. ANALYSIS PROCEDURES

As discussed in Section 2, standard EPA methods of analysis as published in the Federal Register were employed for quantification of the emissions from the absorber and incinerator vents where applicable. To date, no sampling or analytical methods have been promulgated for determination of hydrogen cyanide, acrylonitrile, or acetonitrile in stack gases.

a. Hydrogen Cyanide

The following three methods for analysis of HCN in 0.1N caustic media were considered for the acrylonitrile plant sampling effort:

(1) The National Institute for Occupational Safety and Health (NIOSH) method (P+CAM #116).[40]

(2) Reaction with chloramine-T followed by colorimetric measurements with pyridine-pyrazolone reagent.[41]

(3) Reaction with chloramine-T and nicotinamide followed by fluorometric analysis.[42]

The NIOSH method for HCN in work environments involves collection of HCN with midget impingers containing 15×10^{-6} m^3 of 0.1N NaOH and subsequent measurement of cyanide ion with a specific ion electrode. A detection level of 11 mg HCN/m^3 (9.1 ppm v/v) is attained for a 100-minute sampling period at a 0.001 m^3/min sampling rate. The method is listed by NIOSH as being in general use or approved by most professional industrial hygiene analysts but one that has not been thoroughly evaluated by NIOSH or any of the professional societies. An interference could result from the hydrolysis of α-hydroxynitriles (cyanohydrins) in all three methods discussed here. Partial hydrolysis of these moities could occur in the 0.1N NaOH solution with complete hydrolysis occurring immediately in 0.4N NaOH.

In the colorimetric analysis of HCN by reaction with chloramine-T followed by measurement with pyridine-pyrazolone reagent, the cyanide ion is first converted to cyanogen chloride by chloramine-T. On reaction with the pyridine-pyrazolone reagent a blue dye is formed and absorption read at 630 nm. For extracted color readings the coefficient of variation is 3.9%, the sensitivity is 0.1 μg and the effective range is 0.2 to 2.0 μg.

The fluorometric procedure for HCN proceeds similarly to the colorimetric reaction in that cyanide ion is converted to cyanogen chloride by chloramine-T. The cyanogen chloride then cleaves the pyridine ring of the nicotinamide to produce a product which has a strong blue fluorescence in alkaline media. A plot of fluorescence intensity versus cyanide concentration approximately follows the Baugeur-Beer law. The detection limit of HCN using this procedure is 0.2 microgram of cyanide and the relative standard deviation for the method is ±10% at that level. This method has been employed at the Dayton Laboratory of Monsanto Research Corporation for measurement of thousands of CN^- samples over the past six years. An Aminco-Bowman Spectrophotofluorometer is employed at an excitation wavelength of 365 nm and an emission wavelength of 456 nm.

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[40] Liethe, W. The Analysis of Air Pollutants. Ann Arbor - Humphery Science Publications, Ann Arbor, Michigan, 1970. p. 227. [Used as NIOSH Physical and Chemical Analysis Measurements (P+CAM) Procedure #116.]

[41] Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C., 1971. pp. 404-406.

[42] Hanker, J. S., R. M. Gamson, and H. Klapper. Fluorometric Method for Estimation of Cyanide. Journal of Analytical Chemistry, 29(6):879-871, 1957.

The latter method of analysis for HCN was used for measurement of the acrylonitrile plant samples. The primary basis for this selection is one of cost in analyst time since similar samples are analyzed daily in the Dayton Laboratory and no setup or precalibration is required. The latter method is both more sensitive and accurate than either of the first two methods discussed.

As mentioned previously, α-hydroxynitriles (cyanohydrins) that might be present in the emissions were determined as hydrogen cyanide by this procedure. There was no evidence that α-hydroxynitriles were present in the samples.

Hanker, et al.,[42] have demonstrated that cyano-organophosphorus compounds are retained on passing an air matrix through bubblers filled with diethyl phthalate and that these bubblers pass hydrogen cyanide quantitatively. A sampling train identical in every respect to that presented in Figure J-3 was employed for this measurement, except that diethylphthalate was employed in the first two impingers instead of distilled water. The contents of the two 0.1N KOH impingers were then analyzed for free hydrogen cyanide by the method presented previously.

b. Acrylonitrile and Acetonitrile

Three alternatives have been considered for sampling of acrylonitrile and acetonitrile emissions. These include:

(1) The NIOSH method P+CAM #127.[43]

(2) A variation on the NIOSH method employing porous polymer sorbent rather than activated carbon.[40]

(3) Collection of these species in distilled water.

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[43] White, L. D., D. G. Taylor, P. A. Mauer, and R. E. Kupel. A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere. American Industrial Hygiene Association Journal, 31(2):225-232, 1970. [Used as NIOSH Physical and Chemical Analysis Measurements (P+CAM) Procedure #127.]

The NIOSH method for acrylonitrile and acetonitrile vapors in work environment atmospheres is based on the collection of the organic vapors on activated carbon with subsequent desorption of the species with CS_2 followed by gas chromatographic analyses with a flame ionization detector.[43] The GC/FID approach is common to all three methods considered here. For 0.01 m^3 of sampled air the detection limit for acrylonitrile is 45 mg/m^3 while that for acetonitrile is 70 mg/m^3. This method is rated by NIOSH as a method not used by industrial hygiene analysts but one which gives promise for the determination of organic substances. The drawbacks to using this approach for determination of the nitriles are (1) overloading of the activated carbon due to the high vapor content of the absorber vent stream (5.5 to 11.0 mole %), (2) the variable desorption efficiency for various organic species, and (3) the unknown capacity before breakthrough, especially since water would deactivate adsorption sites. It is projected that an extensive laboratory effort would be required to validate this approach for determination of acrylonitrile plant emissions.

An improvement in this approach would be realized employing porous polymer packings such as Chromasorb 101, Chromasorb 105 or Tenex GC. The sorbents are not affected by water vapor which is passed through without adsorption. In addition, nonpolar and moderately polar organic emissions can be thermally desorbed from the polymer packing without the use of CS_2. This approach, however, would require a laboratory effort to establish adsorption capacity and breakthrough conditions before sampling could be conducted in the field.

The third method involves the collection of the nitrile vapors in distilled water impingers similar to the approach employed for HCN vapors in 0.1N KOH bubblers. Analysis of acrylonitrile and acetonitrile will be performed by gas chromatographic techniques using a Hewlett-Packard HP 5750 Chromatograph with a flame ionization detector. The gas chromatographic column is a 0.9 m x 6.4 mm stainless steel column containing 20% THEED on 250 to 600 μm (30 to 60 mesh) Chromosorb W (acid washed). Acrylonitrile retention time is 1.5 minutes while that for acetonitrile is 2.5 minutes. The detection limits for both nitriles is 50 ppb. The standard deviation for acrylonitrile at this concentration is ±7.7% while the standard deviation for acetonitrile at 0.20 ppm is ±1.8%. As was the case with the HCN analysis recommended, the Dayton Laboratory has conducted several thousand acrylonitrile analyses by the GC-FID approach over the past six years. This approach was used on this program.

c. Carbon Monoxide, Propane, Propylene

Two separate systems were employed to measure CO and hydrocarbon grab samples from the absorber vent. The first approach employed an automated CO, CH_4, total hydrocarbon analyzer developed by Monsanto Research Corporation which measures the three components to a sensitivity of 0.1 ppm. The instrument is a chromatographic system where CO and CH_4 are separated initially by a precolumn. The CO is then reduced to methane over a nickel catalyst and the two time resolved methane peaks determined by by-passing the precolumn and catalyst system and passing a portion of the sample directly to the flame ionization detector.

The second approach employed gas chromatographic techniques with flame ionization detection to identify and quantify the individual hydrocarbon species in the Tedlar bag samples. Here, several options existed:

(a) Direct gas chromatographic analysis with a flame ionization detector.

(b) Analysis by tandem coupled gas chromatograph-mass spectrometer on samples "as received" or concentrated by cryogenic means.

Employing direct chromatographic analysis the low molecular weight hydrocarbons, e.g., methane, ethane, ethylene, propane, propylene and butanes, were identified by retention data and quantified (down to 0.1 ppm) by measuring the response of individual components with a flame ionization detector. Quantification is realized by comparing responses to those of standard gas mixtures. A 3 m x 6.4 mm Porapak Q chromatographic column in tandem with a 3 m x 6.4 mm Porapak R column, or a 0.9 m x 2 mm Carbosieve B column was used in these analyses.

Preliminary examination of a sample indicated a number of unexpected components, and tandem coupled gas chromatography/mass spectrometric analyses were performed to identify the components. The analytical column which was employed for this purpose was a 1.4 m column packed with Porapak Q. Quantitative analysis was conducted by measurement of gas chromatographic peak areas or peak heights of components in the "as received" samples.

d. Analysis of Ambient Air at Acrylonitrile Settling Pond

The analysis approach used was essentially that discussed for analysis of acrylonitrile and acetonitrile. The porous polymer tube was employed to obtain integrated ambient air samples downwind and upwind of the settling pond. The tube was designed so that it was directly interfaceable with a gas chromatograph. Desorption of the collected species was initiated using carrier flow and elevated temperature directly onto the analytical column of the gas chromatograph. Air flow rates of 0.002 m^3/min and a 10-minute sampling time were used and components present at 0.5 $\mu g/m^3$ in the ambient air were measured with a flame ionization detector capable of detecting 10 ng.

GLOSSARY

absorber: Absorption column used to recover acrylonitrile, acetonitrile, hydrogen cyanide, oxygenated hydrocarbons, organic polymers, and other hydrocarbons from the ammonia-free reactor product stream.

acrylonitrile: Colorless, low viscosity organic liquid having the chemical formula, $CH_2 = CHCN$.

affected population: Number of nonplant persons exposed to concentrations of airborne materials which are present in concentrations greater than a determined hazard factor.

ammoxidation: Oxidation of a material in the presence of ammonia.

atmospheric stability class: Class used to designate degree of turbulent mixing in the atmosphere.

Catalyst A: Bismuth/molybdenum catalyst used in the SOHIO process from 1960 to 1967.

Catalyst 21: Depleted uranium catalyst used in the SOHIO process from 1967 through 1973.

Catalyst 41: Catalyst based on bismuth phosphomolybdate and currently (1976) used in the SOHIO process.

criteria pollutant: Emission species for which ambient air quality standards have been established; these include particulates, sulfur dioxide, nitrogen dioxide, carbon monoxide, and nonmethane hydrocarbons (recommended guidelines).

deep well pond: Nonaerated lagoon used for undissolved solids removal from acrylonitrile plant wastewater prior to deep well injection of the wastewater.

emission factor: Weight of material emitted to the atmosphere per unit of acrylonitrile produced, e.g., g material/kg product acrylonitrile.

flare: Combustion device used for the ultimate disposal of small continuous flow hydrocarbon streams and intermittent hydrocarbon streams.

incinerator: Thermal oxidizer used for ultimate disposal of acetonitrile and hydrogen cyanide by-products and plant residues.

noncriteria pollutant: Emission species for which no ambient air quality standards have been established.

product transport loading facility: Facility used at acrylonitrile plants to load product acrylonitrile into railroad tank cars and tank trucks.

quencher: Device used in acrylonitrile manufacture to cool reactor product gases and to remove excess ammonia prior to product recovery in the absorber.

SOHIO process: process for ammoxidation of propylene which is licensed by SOHIO (The Standard Oil Company) for production of acrylonitrile.

source severity: To assess the environmental impact of atmospheric emissions from acrylonitrile manufacture, the source severity for each material emitted from each emission point was estimated. Source severity is defined as the pollutant concentration to which the population may be exposed divided by an "acceptable concentration". The exposure concentration is the time-averaged maximum ground level concentration as determined by Gaussian plume dispersion methodology. The "acceptable concentration" is that pollutant concentration at which an incipient adverse health effect is assumed to occur. For criteria pollutants, it is the corresponding primary ambient air quality standard. For noncriteria pollutants, it is a surrogate air quality standard as determined by reducing TLV's for chemical substances using an appropriate safety factor.

tank outage: Distance from liquid surface to the top of a fixed roof storage tank.

CONVERSION FACTORS AND METRIC PREFIXES[44]

CONVERSION FACTORS		
To convert from	to	Multiply by
degree Celsius (°C)	degree Fahrenheit (°F)	$t^{\circ}_{F} = 1.8\ t^{\circ}_{C} + 32$
degree Kelvin (K)	degree Celsius (°C°	$t^{\circ}_{C} = t^{\circ}_{K} - 273.15$
gram (g)	pound-mass	2.205×10^{-3}
gram/second (g/s)	pounds/hour	7.930
joule (J)	British thermal unit (Btu)	9.479×10^{-4}
kilogram (kg)	pound mass (lb mass avoirdupois)	2.204
kilogram (kg)	ton (short, 2,000 lb mass)	1.102×10^{-3}
kilogram/meter^3 (kg/m^3)	lb mass/foot^3	6.243×10^{-2}
kilometer^2 (km^2)	mile^2	2.591
meter (m)	foot	3.281
meter (m)	inch	3.937×10
meter^3 (m^3)	barrel (42 gal)	6.293
meter^3 (m^3)	foot^3	3.531×10
meter^3 (m^3)	gallon (U.S. liquid)	2.642×10^{2}
meter^3/kilogram (m^{3}kg'	milliliter/gram (ml/g)	1.000×10^{3}
metric ton	pound-mass	2.205×10^{3}
pascal (Pa)	pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES			
Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	1 MJ = 1×10^6 joules
kilo	k	10^3	1 kPa = 1×10^3 pascals
milli	m	10^{-3}	1 mg - 1×10^{-3} gram
micro	μ	10^{-6}	1 m = 1×10^{-6} meter

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[44] Metric Practice Guide. ASTM Designation E 380-74, American Society for Testing and Materials, Philadelphia, Pennsylvania, November 1974. 34 pp.